REACTIONS WITH ELECTROPHILES

OF

COMPLEXES CONTAINING OLEFINIC LIGANDS

by

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Except as recognised in the acknowledgements this thesis is my own original work.

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A C K N O W L E D G E M E N T S

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SUMMARY

This thesis represents an attempt to answer some of the problems arising from work carried out in the years 1961 - 1967 at University College, London, by Drs R.F. Long, G.J. Erskine and W.R. Kneen on gold and platinum complexes of the following *ortho* substituted olefinic tertiary phosphines and arsines:-

(i) *o*-allylphenyldiphenylphosphine,

$(C_6H_5)_2P(o\text{-}C_6H_4CH_2CH{=}CH_2)$, (AP).

(ii) *o*-allylphenyldimethylarsine,

$(CH_3)_2As(o\text{-}C_6H_4CH_2CH{=}CH_2)$, (AA).

(iii) *o*-styryldiphenylphosphine,

$(C_6H_5)_2P(o\text{-}C_6H_4CH{=}CH_2)$, (SP).

(iv) *o*-styryldimethylarsine, $(CH_3)_2As(o\text{-}C_6H_4CH{=}CH_2)$, (SA).

They prepared linear gold(I) complexes of general formula AuBrL in which the double bond of the ligand is uncoordinated, and planar platinum(II) complexes of the same ligands in which the olefinic double bond can be coordinated, as in $PtBr_2L$ (L = ligand), or free as in $PtBr_2L_2$. Bromination of the complexes gives respectively organometallic gold(III) and platinum(IV) complexes containing metal-carbon σ-bonds in chelate rings. X-ray crystallographic studies have shown that

$\overline{AuBr_2[o\text{-}Ph_2PC_6H_4CH(CH_2Br)]}$, "$AuBr_3(SP)$", (*15*d), obtained from AuBr(SP) and bromine, contains a gold-carbon σ-bond

in a five membered chelate ring, whereas bromination of AuBr(AP) gives a six membered σ-bonded chelate ring complex $\overline{AuBr_2[o\text{-}Ph_2PC_6H_4CH(CH_2Br)CH_2}]$, "$AuBr_3(AP)$", (*15*a). On alcoholysis the bromination products undergo nucleophilic substitution of the bromine atom in the chelate ring and an X-ray structure determination has shown that

$\overline{PtBr_3[o\text{-}Me_2AsC_6H_4CHOEtCH_2}][o\text{-}Me_2AsC_6H_4CH{=}CH_2]$

"$PtBr_3(SAOEt)(SA)$", (*6*c), contains a six membered chelate ring. This work has been extended as follows:-

(i) The complex of formula $PtBr_4(SA)_2$, obtained from bromine and $PtBr_2(SA)_2$, is an inseparable mixture one component of which is probably the five membered σ-bonded chelate ring complex

$\overline{PtBr_3[o\text{-}Me_2AsC_6H_4CH(CH_2Br)}]\cdot[o\text{-}Me_2AsC_6H_4CH{=}CH_2]$ (*3*c).

Chromatography of (*3*c) on silica-gel gives the new hydroxy complex $\overline{PtBr_3[o\text{-}Me_2AsC_6H_4CHOHCH_2}][o\text{-}Me_2AsC_6H_4CH{=}CH_2]$, "$PtBr_3(SAOH)(SA)$", (*19*c), probably containing a six membered chelate ring.

(ii) By comparison with the nmr spectrum of (*6*c) it is shown that the alcoholysis products of $AuBr_3(SP)$ (*15*d) contain six membered chelate rings,

e.g. $\overline{AuBr_2[o\text{-}PPh_2C_6H_4CHOEtCH_2}]$, "$AuBr_2(SPOEt)$", (*16*d), as originally suggested by Kneen. (*15*d) undergoes nucleophilic substitution with glacial acetic acid and

water giving the new complexes $\overline{AuBr_2[o\text{-}PPH_2C_6H_4CHRCH_2}]$, R = $OCOCH_3$,OH, abbreviated to "$AuBr_2(SPOCOCH_3)$" (*21*d) and "$AuBr_2(SPOH)$" (*20*d) respectively.

(iii) Chlorination of the gold(I) complex AuCl(SP) gives a six membered σ-bonded chelate ring gold(III) complex $\overline{AuCl_2[o\text{-}PPh_2C_6H_4CHClCH_2}]$, "$AuCl_3(SP)$", (*22*d), which also undergoes nucleophilic substitution with alcohols and acetic acid giving $\overline{AuCl_2[o\text{-}PPh_2C_6H_4CHRCH_2}]$, R = OCH_3, OC_2H_5, $OCOCH_3$. The latter products and the corresponding new bromo complexes (*21*d) and (*20*d) are all shown to contain six membered chelate rings.

(iv) Addition of bromine to AuBr(SP) to give (*15*d) probably proceeds *via* an intermediate tribromo gold(III) complex identified by its nmr spectrum. The solvolyses of $AuCl_3(SP)$ (*22*d) and $AuBr_3(SP)$ (*15*d) and the conversion of $AuBr_2(SPOH)$ (*20*d) to (*15*d) may involve the same intermediate; other possible mechanisms are also discussed.

(v) As shown by Kneen, alcoholysis of (*15*a) gives a pair of isomers but it has not been possible to assign their structures with certainty, although some additional possible structures are suggested.

C O N T E N T S

CHAPTER I

A review of the formation and reaction of gold(III) and platinum(IV) organometallic compounds containing ligands derived from o-substituted tertiary phosphines and arsines.

1. The reaction of organometallic and coordination compounds with halogens

2. Previous work carried out on platinum and gold complexes derived from o-substituted tertiary phosphines and arsines

3. Problems arising from the work on gold and platinum olefinic tertiary phosphine and arsine complexes

4. Numbering system for the gold and platinum olefinic tertiary phosphine and arsine complexes in Chapter I

1. The reaction of organometallic and coordination compounds with halogens.

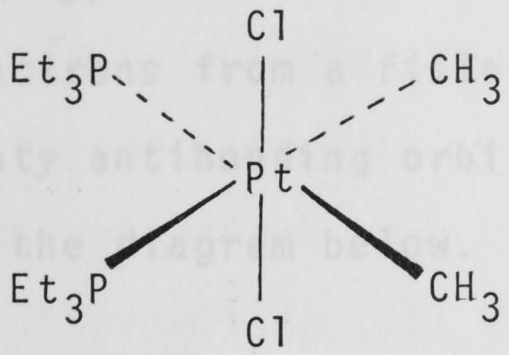
Since this thesis deals with the preparation and halogenation of transition metal organo-phosphorus and arsenic complexes, and the properties of the organometallic products formed on halogenation it is intended to review briefly organometallic compounds and the reaction of these and other metal complexes with halogens, particularly those compounds containing olefinic double bonds.

(A) Organometallic compounds.

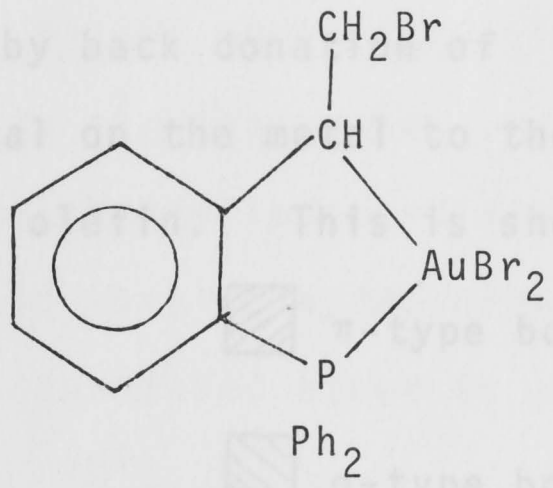
Organometallic compounds can be defined as those compounds containing a direct metal-carbon linkage. However, since it is difficult to define a metal precisely, they are usually defined as compounds containing anionic carbon, or carbon σ-bonded to a more electropositive element. This electronic statement limits the term "organometallic compound" to carbon derivatives of Groups I-III, the later elements of Groups IV and V, and to any organic derivative of a transition metal containing an ionic or σ-carbon metal bond.

Organometallic compounds contain many different types of metal-carbon bond. For example, metals of Group I tend to form compounds in which the metal-carbon bond is mainly ionic, n-butyl sodium, Na^{+} n-$C_4H_9^{-}$, and phenyl sodium, $C_6H_5^{-}Na^{+}$, [1] being typical examples. The transition elements however contain metal-carbon bonds

that are covalent σ-bonds. Examples are the *trans*-bis [(triethylphosphine)dichloro (dimethyl)] platinum[2] (A) and a gold(III) complex containing a metal-carbon σ-bond in a chelate ring, $AuBr_3(SP)$,[3] (*15*d), which is described later.

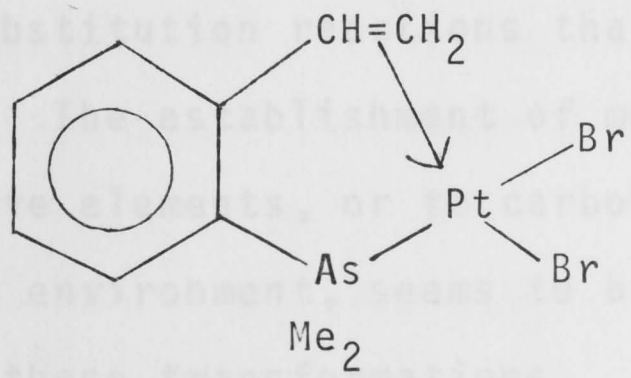


(A)



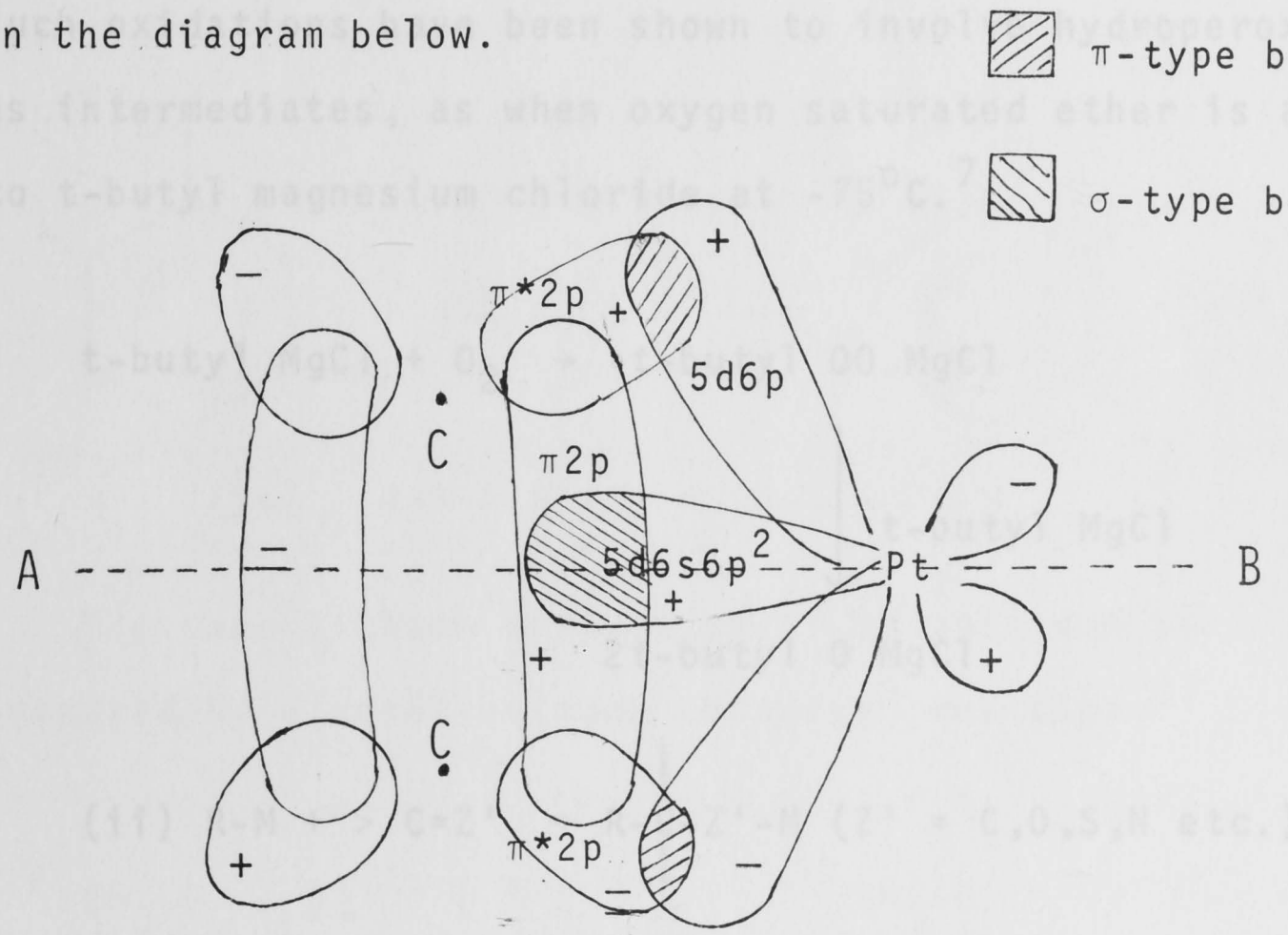
(*15*d)

Organometallic compounds also include those in which the metal is bonded to the organic ligand via an olefinic bond, although these are limited to complexes of transition metals which have the necessary orbitals available for bonding, as explained below. The chelate platinum(II) complex $PtBr_2(SA)$[4] (*8*c) which will also be discussed later, is an example.



(*8*c)

Using a model originally proposed by Dewar[5] for silver metal-olefin complexes, Chatt[6] proposed that bonding in platinum metal-olefin complexes occurs via a σ-type bond formed by donation of electrons from the π-bonding orbital of the olefin to an empty $5d6s6p^2$ orbital on the metal. A π-type of bond is also formed by back donation of electrons from a filled dp orbital on the metal to the empty antibonding orbital on the olefin. This is shown in the diagram below.



The carbon-metal bond participates in a wide variety of addition and substitution reactions that are summarised below. The establishment of metal bonds to more electronegative elements, or to carbon in a more anionically stable environment, seems to be the driving force for most of these transformations.

(a) Addition.

(i) $R\text{-}M + Z \rightarrow R\text{-}Z\text{-}M$, $(Z=O, S, R'_mM.)$

With the notable exception of mercury alkyls, all the metal alkyls of Groups I-III suffer air oxidation of their carbon-metal bonds and, if the metal alkyl is sufficiently volatile, exposure to air can cause spontaneous burning. Under more controlled conditions, such oxidations have been shown to involve hydroperoxides as intermediates, as when oxygen saturated ether is added to t-butyl magnesium chloride at $-75^{o}C$.[7]

t-butyl MgCl + O_2 → t-butyl OO MgCl

↓ t-butyl MgCl

2t-butyl O MgCl.

(ii) $R\text{-}M + > C{=}Z' \rightarrow R\text{-}\underset{|}{\overset{|}{C}}\text{-}Z'\text{-}M$ (Z' = C,O,S,N etc.)

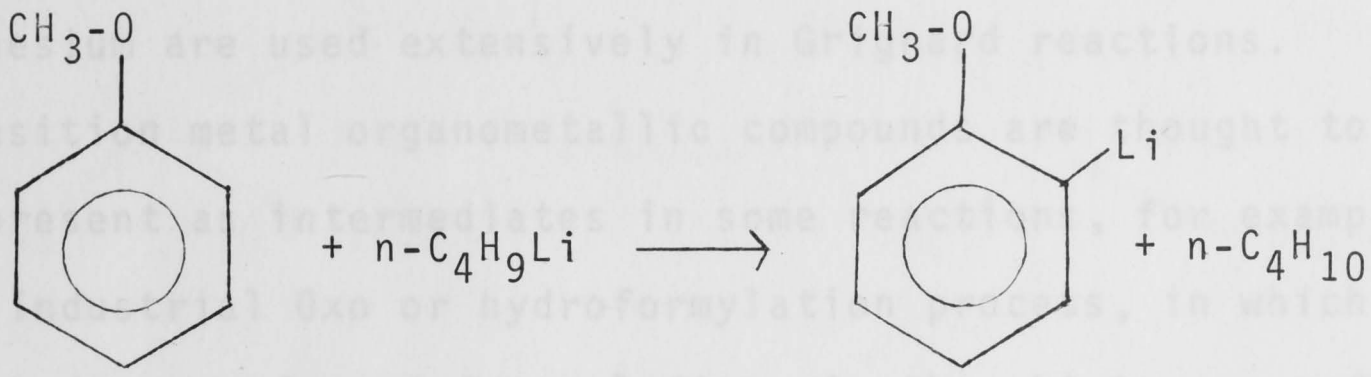
The organometallic compounds of Groups 1A, 11A and 111A, in particular the aluminium alkyls, undergo addition with olefins and acetylenes. Ethylene will undergo addition with triethyl aluminium under pressure.[8]

$$(CH_3CH_2)_3Al \xrightarrow[\Delta/\text{pressure}]{CH_2=CH_2} [CH_3CH_2(CH_2CH_2)_n]_3Al$$

(b) Substitution

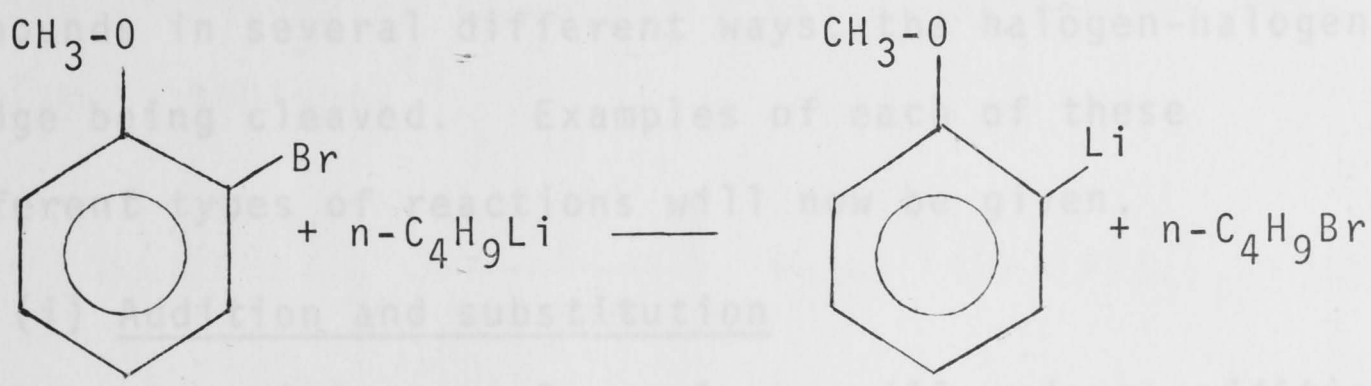
(iii) $R\text{-}M + R'\text{-}H \rightarrow R\text{-}H + M\text{-}R'$

In this type of reaction, usually called metal-hydrogen exchange or metalation,[9] an organic pseudo- or Brønsted acid containing an active C-H bond undergoes reaction to form a new carbon-metal bond, as when n-butyl lithium is added to anisole.[10]



(iv) $R\text{-}M + R'\text{-}X \rightarrow R\text{-}X + R'\text{-}M$

The same lithium derivative of anisole can be prepared by a metal-halogen exchange[9] reaction.[11]



(v) $R\text{-}M + M'\text{-}R' \longrightarrow R'\text{-}M + M'\text{-}R$

In these metal-metal exchange reactions,[12,13] metal alkyls will undergo exchange in which the more

electropositive metal tends to become associated with the more electronegative organic group, as in this boron-aluminium exchange reaction.[14]

$$(C_6H_5CH_2)_3B + (CH_3CH_2)_3Al \rightleftharpoons (CH_3CH_2)_3B + (C_6H_5CH_2)_3Al$$

The reactivity of the carbon-metal bond makes organometallic compounds particularly useful in organic synthesis, for example the organometallic compounds of magnesium are used extensively in Grignard reactions. Transition metal organometallic compounds are thought to be present as intermediates in some reactions, for example the industrial Oxo or hydroformylation process, in which aldehydes are formed from olefins, is thought to proceed via an acyl tetracarbonyl complex.[15]

(B) Halogenation

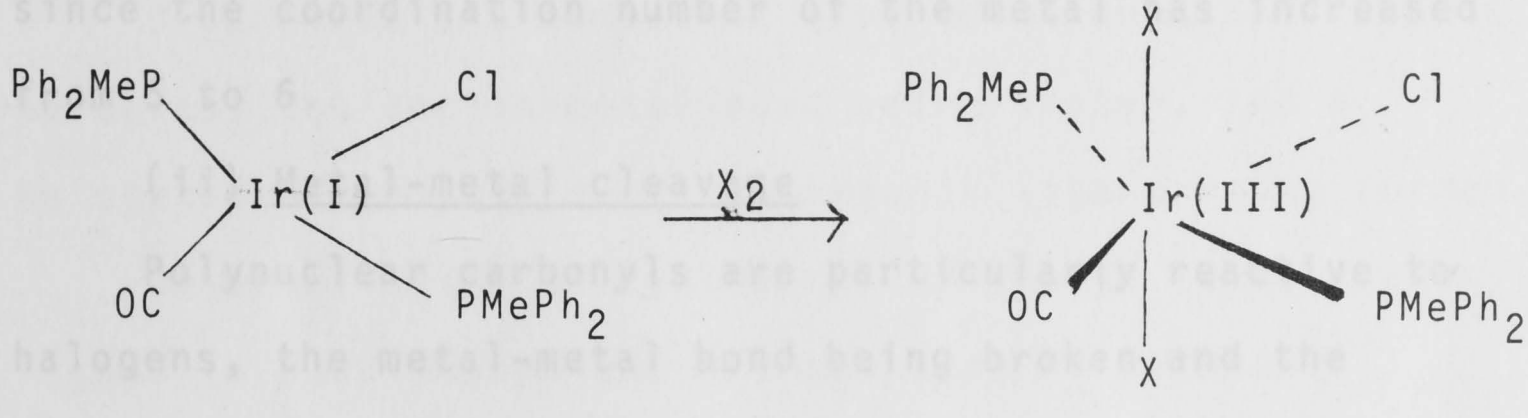
Halogens react with organometallic and coordination compounds in several different ways, the halogen-halogen bridge being cleaved. Examples of each of these different types of reactions will now be given.

(i) Addition and substitution

Many transition metal complexes will undergo addition reactions with halogens, the cleaved halogen adding to the metal atom or ion in the complex. Since the metal atom or ion is oxidised during the addition, this type of reaction is known as "Oxidative - Addition." It

particularly applies to complexes of metals having a d^8 electronic configuration, (e.g. Pt(II), Os(0), Ir(I)), that are converted to complexes having a d^6 configuration through the addition of a covalent halogen molecule.[16]

For example the planar four-coordinate Ir(I) complex (B) is oxidised to the octahedral Ir(III) complex (C) in the presence of halogens,[17] the phosphines remaining in the *trans*-position.



(B) (C)

(X = Cl, Br, I)

Substitution occurs when one or more ligands is replaced by a halogen atom, as when the square planar platinum(II) complex *trans* $PtHCl(PEt_3)_2$ is treated with bromine in benzene.[18]

$$trans\ PtHCl(PEt_3)_2 \xrightarrow[\text{benzene}]{Br_2} trans\ PtBr_2(PEt_3)_2 + HCl.$$

In this case the ligand being replaced has a similar charge to the halogen, so the metal ion remains in its original oxidation state. If however a neutral ligand is replaced by a halogen atom, the metal atom or ion is

oxidised. For example when a carbonyl ligand in (D) is replaced by two halogen atoms to give (E).[19]

$$(\pi\text{-}C_5H_5)M(CO)_3X \xrightarrow[\text{chloroform}]{X_2} (\pi\text{-}C_5H_5)M(CO)_2X_3$$

(D) (E)

(X = Cl, Br, I; M = Mo, W.)

In this reaction oxidative-addition has also occurred since the coordination number of the metal has increased from 5 to 6.

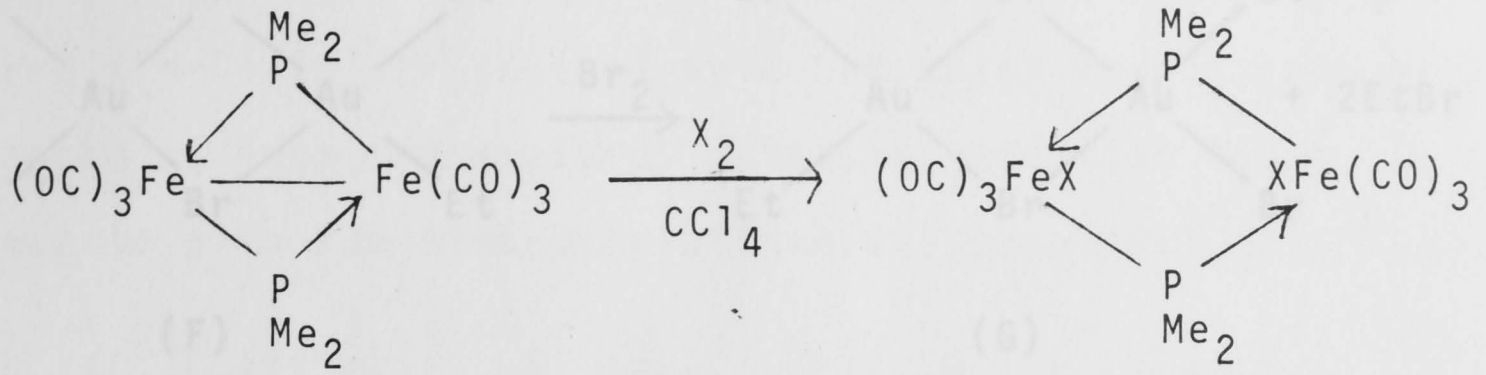
(ii) Metal-metal cleavage

Polynuclear carbonyls are particularly reactive to halogens, the metal-metal bond being broken and the monomeric derivative being formed.

Cyclopentadienyl molybdenum tricarbonyl dimer reacts with iodine in methylene dichloride to form cyclopentadienyl molybdenum tricarbonyl iodide.[20]

$$[(\pi\text{-}C_5H_5)Mo(CO)_3]_2 \xrightarrow{I_2} (\pi\text{-}C_5H_5)Mo(CO)_3I.$$

Addition of chlorine, bromine or iodine to the phosphito-bridged iron complex $[Fe\{(P(CH_3)_2\}(CO)_3]_2$ breaks the Fe-Fe bond, the phosphorus metal bonds remaining intact.[21]



(X = Br, Cl, I)

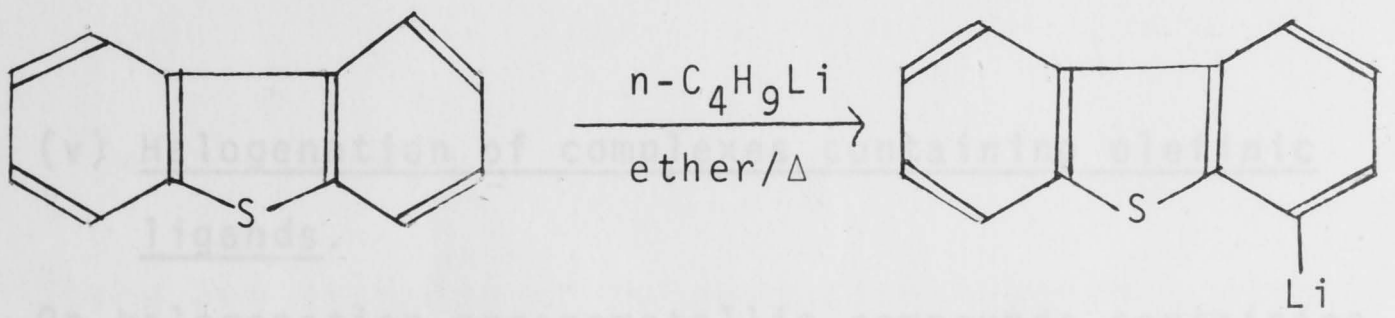
(iii) Metal-carbon cleavage.

Organometallic compounds tend to be unstable towards halogens, the carbon-metal bond being broken, and a halogenated derivative of the organic ligand being formed.

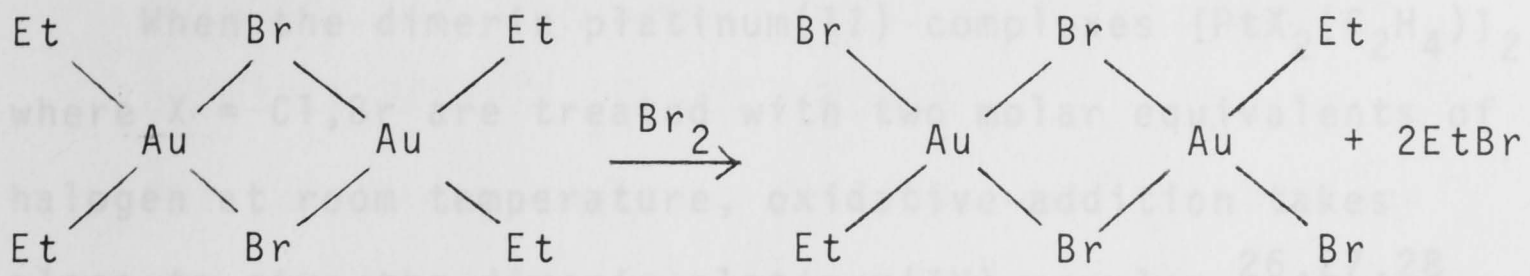
On bromination of cyclohexyl triphenyl lead, a phenyl ligand is substituted and bromobenzene is formed.[22]

$$(C_6H_{11})(Ph)_3Pb + Br_2 \longrightarrow (C_6H_{11})(Ph)_2BrPb + PhBr$$

This type of reaction can be useful in organic synthesis, for example the preparation of 4-iododibenzothiophene via a metalation route using lithium.[23]



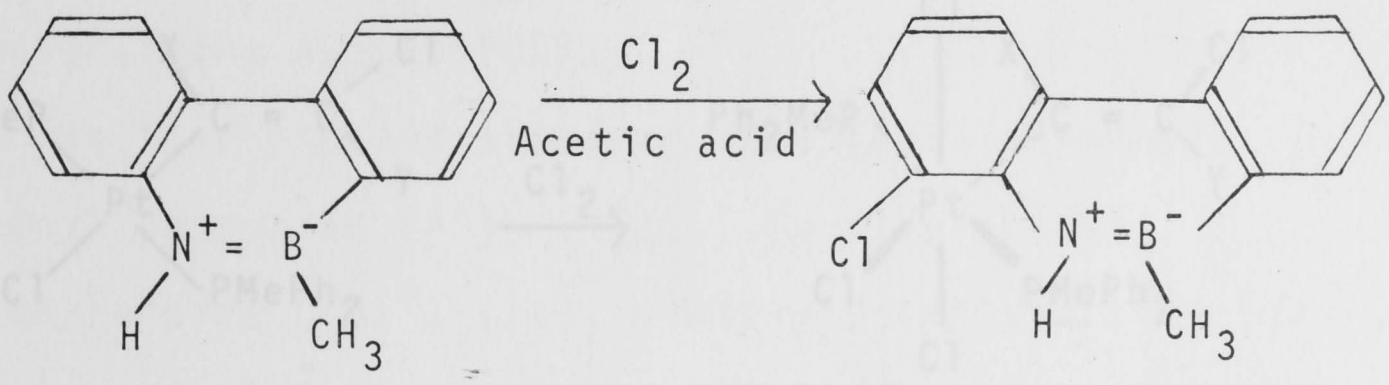
When the dimeric bromo(diethyl)gold(III) complex (F) is treated with bromine in carbon tetrachloride, cleavage of two gold-carbon bonds occurs to give the substituted complex (G).[24]



(F) (G)

(iv) Substitution in the organic ligand

Very few examples are known of reactions in which the halogen will react with the organic ligand without affecting the carbon-metal bond. However it has been found that treatment of 10-methyl-10:9-borazarophenanthrene with one equivalent of chlorine, gives a product in which chlorination has occurred in one of the rings.[25]



(v) Halogenation of complexes containing olefinic ligands.

On halogenation organometallic compounds containing olefinic ligands tend to undergo oxidative-addition, then cleavage of the carbon-metal bond with excess halogen.

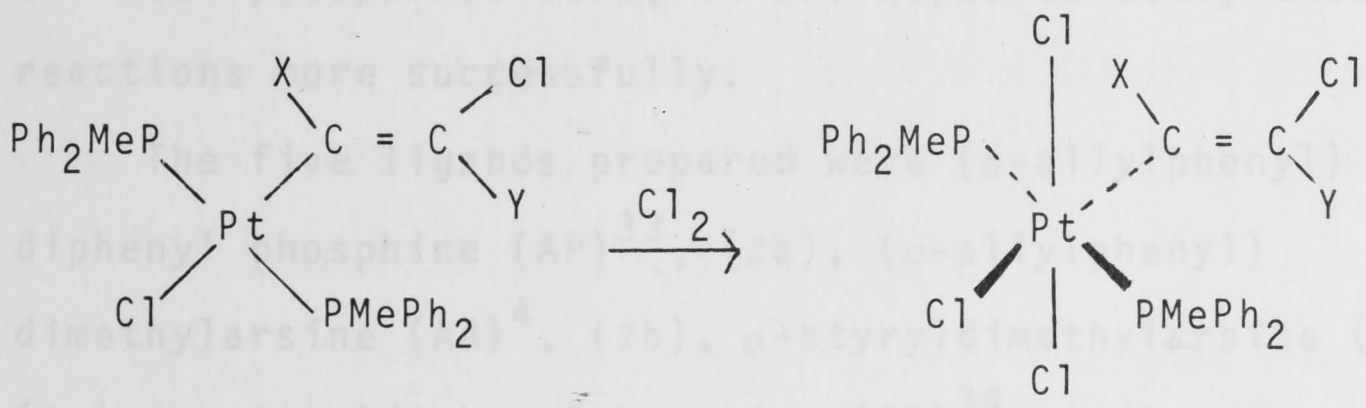
When the dimeric platinum(II) complexes $[PtX_2(C_2H_4)]_2$, where X = Cl,Br are treated with two molar equivalents of halogen at room temperature, oxidative-addition takes place to give the dimeric platinum(IV) complex.[26,27,28]

e.g. $[(C_2H_4)Pt\ Cl_2]_2 + 2Br_2 \rightarrow [(C_2H_4)Pt\ Cl_2Br_2]_2$

On refluxing with excess halogen however, the carbon-metal bonds are broken and the halogenated olefin is formed.

e.g. $[(C_2H_4)Pt\ Cl_2]_2 + 2Br_2 \rightarrow 2C_2H_4Br_2 + 2PtCl_2$

It has been found recently that treatment of the chlorovinyl platinum(II) complex (H) with the stoichiometric amount of chlorine causes oxidation to the octahedral platinum(IV) complex (I).[29]



(H) (I)

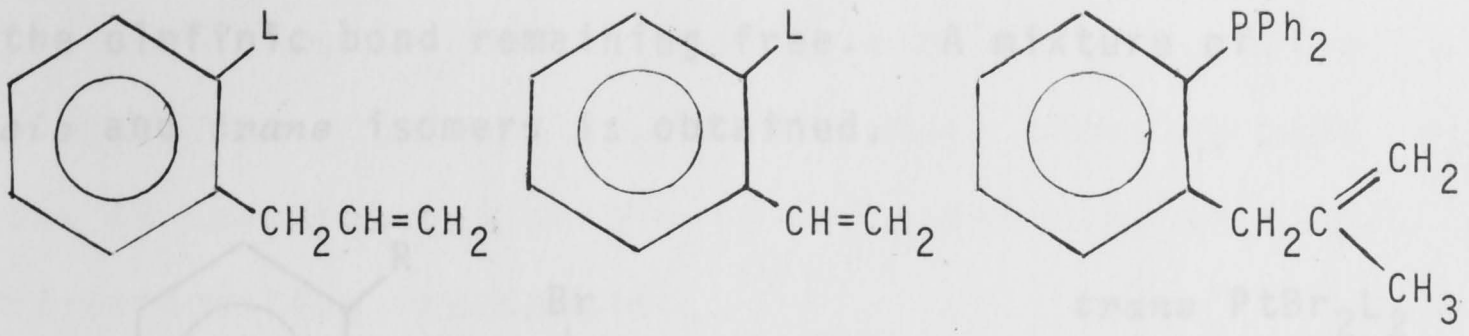
(X = Cl,H; Y = Cl,H)

There are examples of halogenation reactions with complexes, containing olefinic ligands bonded to the metal through a phosphorus or arsenic atom, that prove to be more stable to bond cleavage. However these will be dealt with later.

2. Gold and platinum complexes of *ortho*-substituted tertiary phosphines and arsines

This section summarises previous work on gold and platinum complexes of *ortho*-substituted tertiary phosphines and arsines carried out by Long, Erksine and Kneen.[30,31,32] These complexes were prepared in order to study the reactivity of coordinated ligands, in particular the halogenation of the double bond when it is either coordinated to, or in the vicinity of, the transition metal atom. Previous attempts to study the reactivity of the olefinic bond towards halogens in organometallic compounds had been unsuccessful, as halogenation tended to cause cleavage of the carbon-metal bond. By using olefinic ligands bonded to the metal by a more stable metal-arsine or metal-phosphorus bond, it was hoped to study these reactions more successfully.

The five ligands prepared were (*o*-allylphenyl) diphenyl phosphine (AP)[33], (*1*a), (*o*-allylphenyl) dimethylarsine (AA)[4], (*1*b), *o*-styryldimethylarsine (SA)[4], (*1*c), *o*-styryldiphenylphosphine (SP)[34], (*1*d) and (*o*-methallylphenyl)diphenylphosphine (MP), (*1*e)[35].



(*1*)

(a) L = PPh_2 (AP) (c) L = $AsMe_2$ (SA) (e) MP

(b) L = $AsMe_2$ (AA) (d) L = PPh_2 (SP)

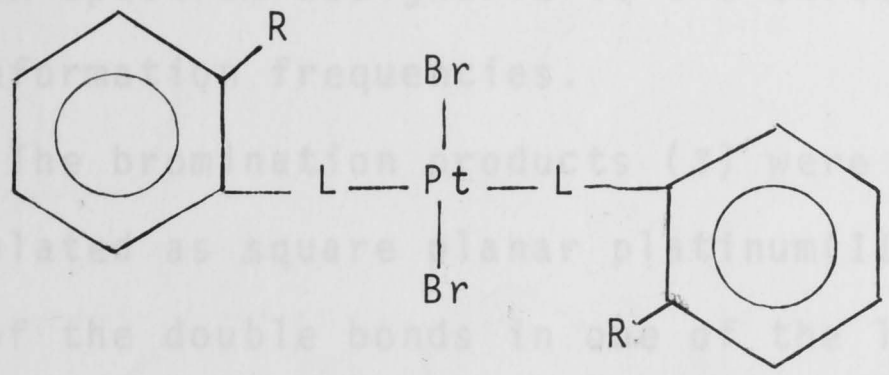
(A) Platinum olefinic tertiary phosphine and arsine complexes.

It was found that these ligands formed two types of complex with divalent platinum. In the complexes of general formula PtX_2 (ligand), (X = Cl,Br and I), both the double bond and the Group V donor atom are attached to the metal, whereas in the bis-ligand complexes exemplified by $PtBr_2$ $(ligand)_2$ only the Group V donor atoms are coordinated, the double bonds remaining free.

(i) Complexes of the type PtX_2L_2.

Long, Erskine[4] and Kneen[34] found that when two moles of the tertiary arsines and phosphines SA, AA or AP are added to anhydrous platinous dibromide in chloroform, pale yellow solids of formula $PtBr_2L_2$ (*2*), (L = SA,AA,AP) are obtained. These show a band at *ca* 1640 cm^{-1} in the IR spectrum due to an uncoordinated C=C stretching frequency[36] and are therefore formulated as square planar platinum(II) complexes in which the ligands are coordinated through the phosphorus or arsenic atoms,

the olefinic bond remaining free. A mixture of *cis* and *trans* isomers is obtained.



trans $PtBr_2L_2$

(2)

(a) R = CH_2-CH=CH_2, L = PPh_2.....$PtBr_2(AP)_2$

(b) R = CH_2-CH=CH_2, L = $AsMe_2$.....$PtBr_2(AA)_2$

(c) R = CH=CH_2, L = $AsMe_2$ .....$PtBr_2(SA)_2$

When L is SA or AA, addition of one mole of bromine to (*2*) gives yellow crystalline complexes of formula $PtBr_4L_2$ (*3*). These differ from the product obtained by the addition of one mole of bromine to the corresponding arsine complex $PtBr_2(AsMePh_2)_2$, which gives an orange crystalline complex $PtBr_4(AsMePh_2)_2$,[31] in which oxidation-addition has taken place at the platinum atom, the orange colour being characteristic of a platinum(IV) complex. The IR spectrum of the complexes (*3*) show the uncoordinated C=C frequency as a very weak band at *ca* 1640 cm^{-1}, and the characteristic vinyl frequencies are either shifted, or appear with reduced intensity compared with the original platinum(II) complexes (*2*).

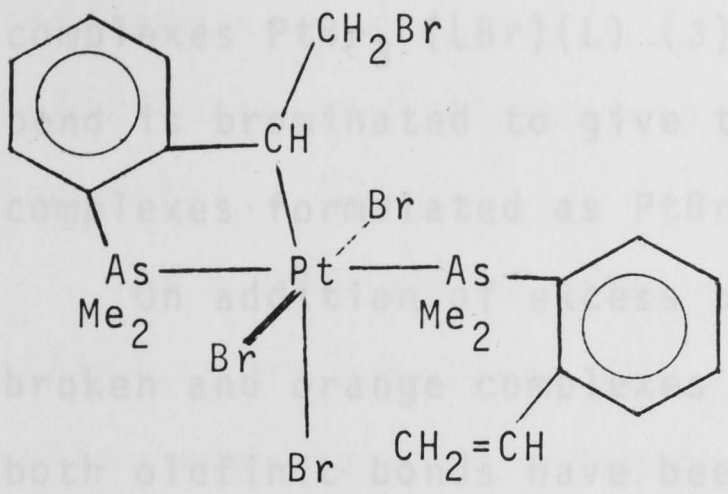
Addition of a further mole of bromine gives a yellow crystalline complex $PtBr_6L_2$ (*4*), which shows no band in the IR spectrum assignable to C=C stretching or vinyl CH deformation frequencies.

The bromination products (*3*) were therefore originally formulated as square planar platinum(II) complexes in which one of the double bonds in one of the ligands had been brominated, i.e. Pt $Br_2(L)(LBr_2)$.[31] Addition of a further mole of bromine would brominate the remaining double bond to give Pt Br_2 $(LBr_2)_2$, and excess bromine would eventually oxidise the platinum atom to give Pt $Br_4(LBr_2)_2$.

However, on further investigation,[4] it was found that the end-product of the bromination of $PtBr_2L_2$ (*2*), the orange platinum complex $PtBr_4(LBr_2)_2$ (*5*), is reduced by tin(II) chloride to the corresponding platinum(II) complex $PtBr_2$ $(LBr_2)_2$, which is not identical with the complex $PtBr_6$ $(L)_2$ (*4*) obtained by adding two equivalents of bromine to $PtBr_2$ $(L)_2$ (*2*).

The initial bromination product (*3*) was therefore reformulated as an octahedral platinum(IV) complex containing a Pt-C σ-bond in a chelate ring, one bromine atom having added to the metal and one to the double bond, written as $PtBr_3$ (L)(LBr). The complex $PtBr_3$(SA)(SABr), (*3*c), could contain a five membered or a six membered chelate ring as shown. However nmr evidence will be

presented later to show that the five membered chelate ring is the most probable, as in (3cI).



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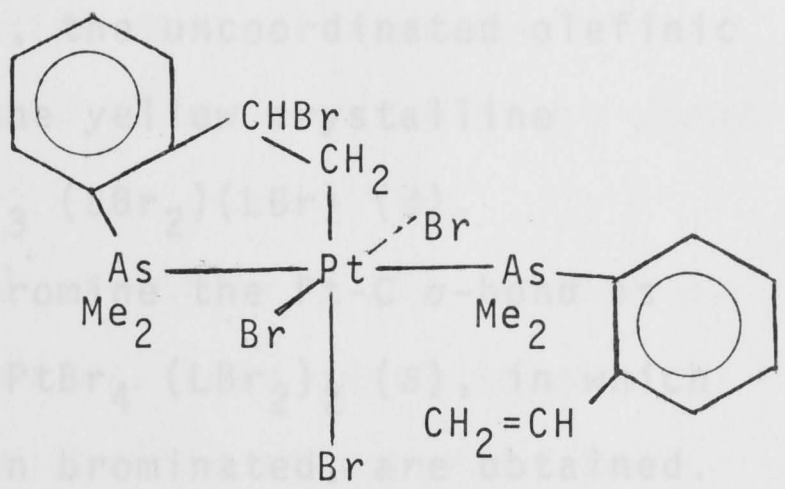
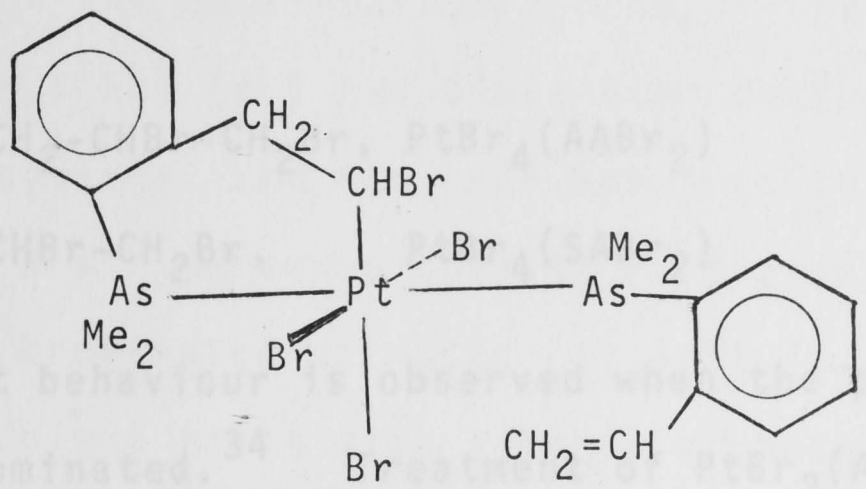


(II)

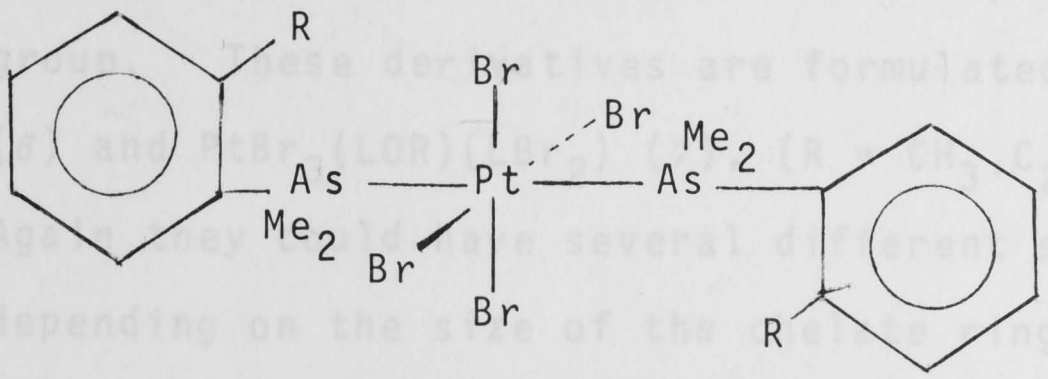


(III)

Similarly the complex $PtBr_3$ (AABr)(AA) could contain a five, six or seven membered chelate ring.

When a further mole of bromine is added to the complexes $PtBr_3$ (LBr)(L) (*3*), the uncoordinated olefinic bond is brominated to give the yellow crystalline complexes formulated as $PtBr_3$ $(LBr_2)(LBr)$ (*4*).

On addition of excess bromine the Pt-C σ-bond is broken and orange complexes $PtBr_4$ $(LBr_2)_2$ (*5*), in which both olefinic bonds have been brominated, are obtained.



(*5*)

(b) R = CH_2-CHBr-CH_2Br, $PtBr_4(AABr_2)$

(c) R = CHBr-CH_2Br, $PtBr_4(SABr_2)$

Different behaviour is observed when the phosphine complex is brominated.[34] Treatment of $PtBr_2(AP)_2$ with one equivalent of bromine in benzene, gives only the chelate olefin complex $PtBr_2(AP)$ (*8*a) in good yield, instead of the octahedral platinum(IV)-carbon σ-bonded complexes obtained on bromination of the arsine complexes. However bromination of the arsine complex $PtBr_2(AA)_2$ in more polar solvents does give the chelate complex $PtBr_2(AA)$ (*8*b), and this is also formed as a by-product

in the reaction of $PtBr_4(AA)_2$ with alcohols. This instability of the platinum(IV)-carbon σ-bonded complex in the diphenyl-phosphino series is probably due to steric difficulties involved in fitting two bulky *ortho*-substituted aryl phosphines and three bromine atoms about the metal.

On refluxing in methanol or ethanol, the octahedral platinum(IV) complexes (*3*) and (*4*) both react to give yellow complexes in which the bromine attached to the carbon in the chelate ring has been replaced by an alkoxy group. These derivatives are formulated as $PtBr_3(LOR)(L)$ (*6*) and $PtBr_3(LOR)(LBr_2)$ (*7*), ($R = CH_3, C_2H_5$) respectively. Again they could have several different structures depending on the size of the chelate ring and the position of attachment of the metal-carbon σ-bond. The structure of $PtBr_3(SAOC_2H_5)(SA)$ (*6*c) has since been determined by X-ray crystallography[3] and has been shown to contain a Pt-C σ-bond in a six membered chelate ring (see page 21).

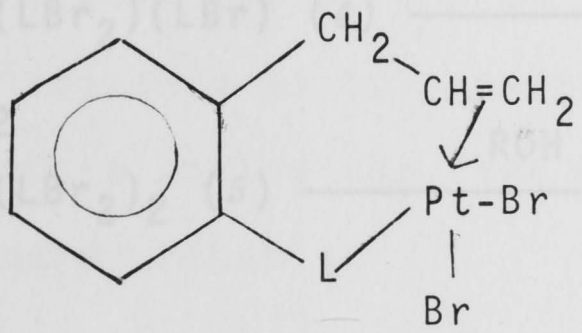
The fully brominated products (*5*) that do not contain a Pt-C σ-bond do not react with ethanol or methanol.

The bromination and alcoholysis reactions are summarised in a flow chart on page 21.

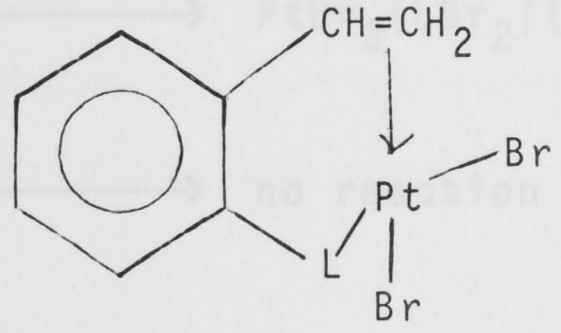
(ii) Complexes of the type PtX_2L.

When one equivalent of each of the ligands SA, AA, SP, AP or MP is added to platinous dibromide in chloroform, crystalline complexes of general formula $PtBr_2$(ligand) are obtained.[34,37] These are colourless, non-conducting in

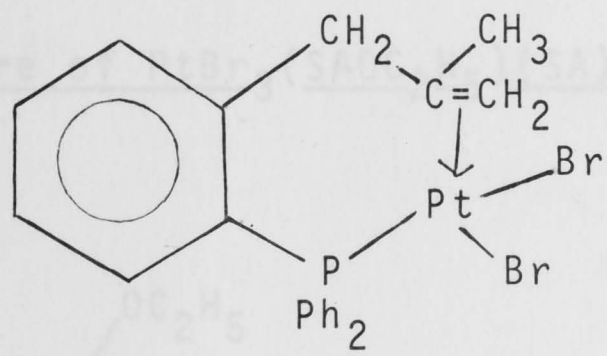
nitrobenzene and their IR spectrum shows no band at *ca* 1640 cm^{-1} due to an uncoordinated C=C stretching frequency.[36] Instead a new band appears at *ca* 1490 cm^{-1} which is characteristic of a C=C stretching frequency modified by coordination to platinum.[6,38] These complexes are therefore formulated as square planar platinum chelate complexes (*8*) as shown.



(*8* a,b)



(*8* c,d)



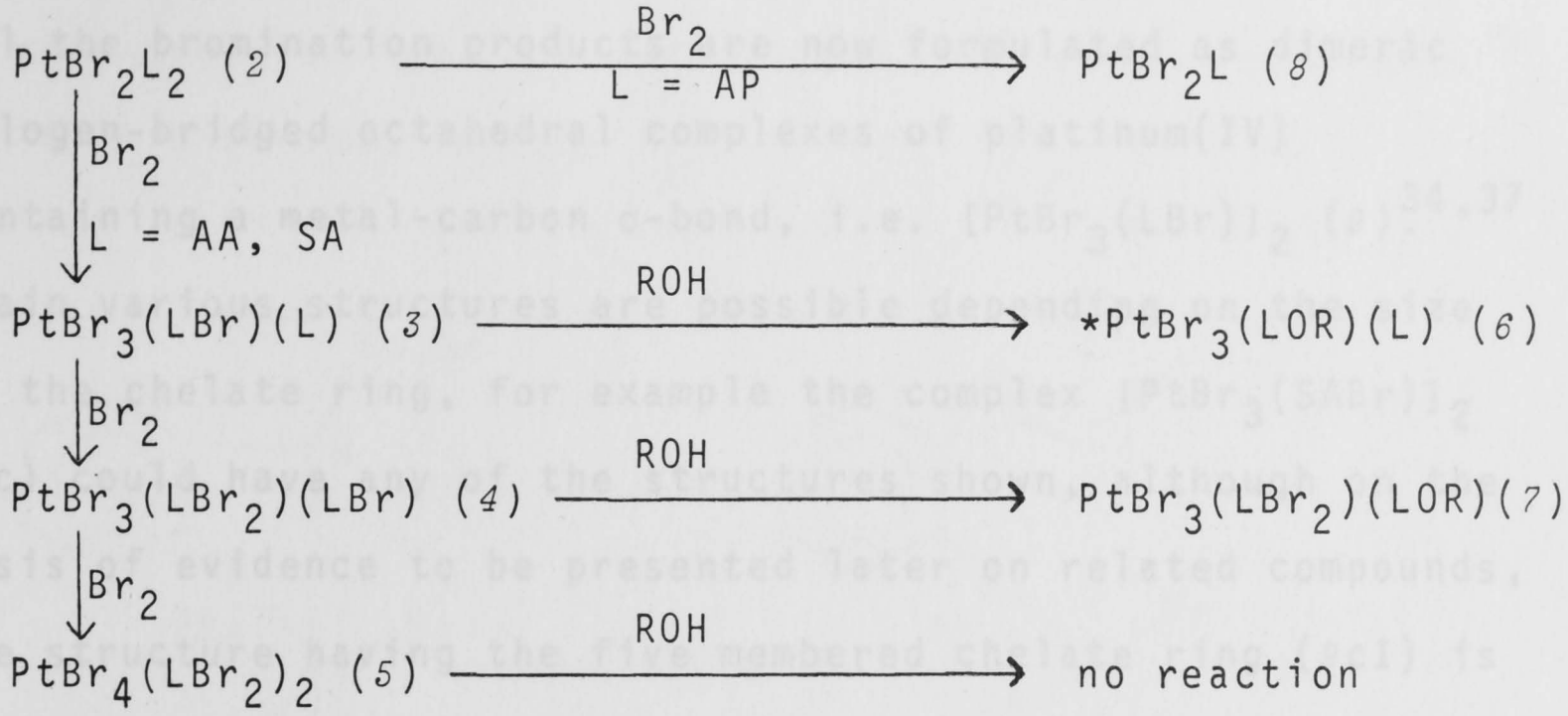
(*8* e)

(a) L = PPh_2 (c) L = $AsMe_2$ (e) $PtBr_2$(MP)

(b) L = $AsMe_2$ (d) L = PPh_2

All the chelate complexes except $PtBr_2$(MP) react with one equivalent of bromine to give orange complexes of general formula $PtBr_4$(ligand). Originally the arsine complexes were formulated as dimeric halogen-bridged platinum(II) complexes in which both double bonds were

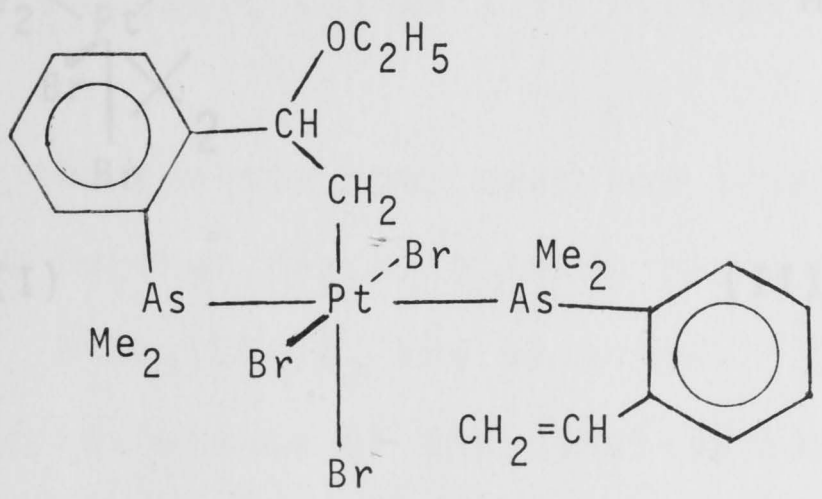
Bromination of the bis-ligand complexes $PtBr_2L_2$



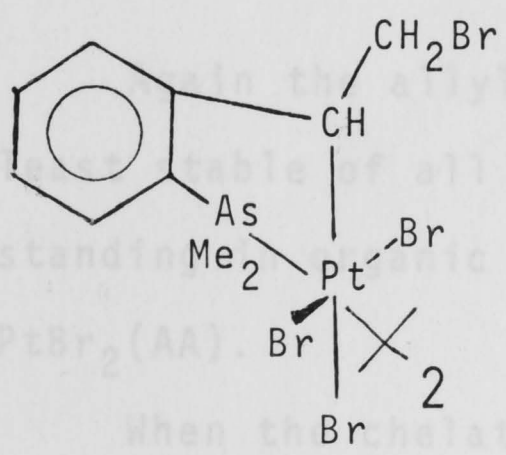
* plus $PtBr_2(AA)$ when L = AA.

R = CH_3 or C_2H_5 for all reactions.

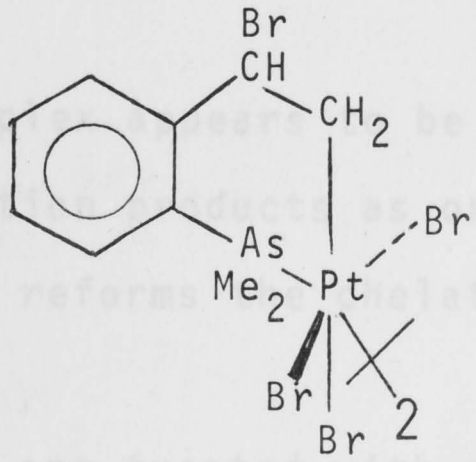
Structure of $PtBr_3(SAOC_2H_5)(SA)$.



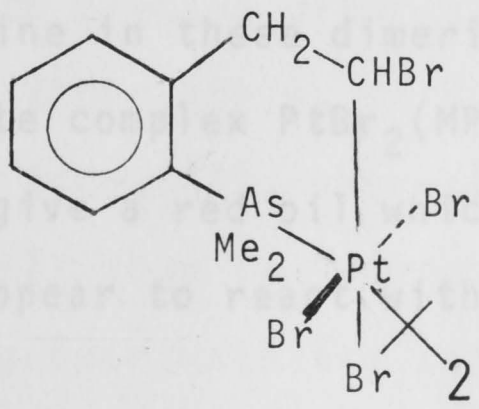
brominated, i.e. $[PtBr_2(LBr_2)]_2$.[31] However by comparison with the previous work on bromination of the PtX_2L_2 complexes, all the bromination products are now formulated as dimeric halogen-bridged octahedral complexes of platinum(IV) containing a metal-carbon σ-bond, i.e. $[PtBr_3(LBr)]_2$ (*9*).[34,37] Again various structures are possible depending on the size of the chelate ring, for example the complex $[PtBr_3(SABr)]_2$ (*9*c) could have any of the structures shown, although on the basis of evidence to be presented later on related compounds, the structure having the five membered chelate ring (*9*cI) is thought more probable.



(I)

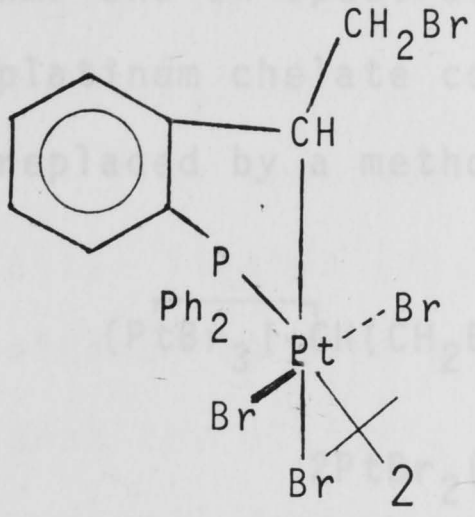


(II)

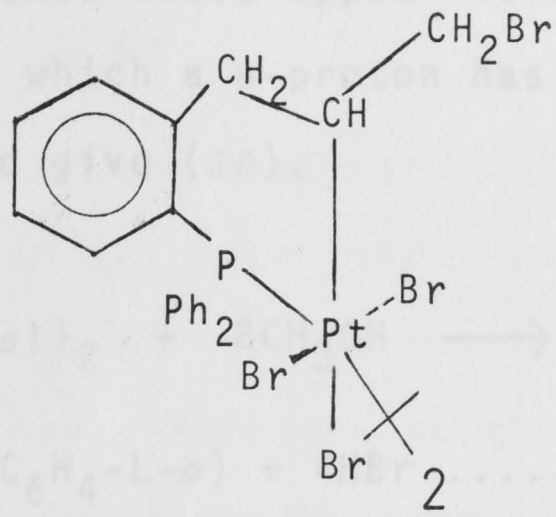


(III)

The phosphine complexes are thought to have the structures shown in (9d) and (9a) by analogy with the known structures of some similar gold(III) SP and AP complexes[39] to be discussed later.



(9d) $[PtBr_3(SPBr)]_2$



(9a) $[PtBr_3(APBr)]_2$

Again the allyl arsine complex appears to be the least stable of all the bromination products as on standing in organic solvents it reforms the chelate $PtBr_2(AA)$.

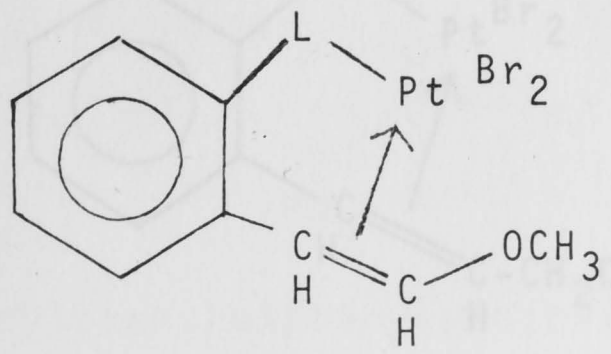
When the chelate complexes are treated with excess bromine no further reaction takes place and the same complexes $[PtBr_3(LBr)]_2$ are obtained. This shows the remarkable resistance of the metal-carbon σ-bonds to attack by bromine in these dimeric complexes.

The chelate complex $PtBr_2(MP)$ reacts with bromine in benzene to give a red oil which cannot be crystallised and does not appear to react with alcohols.

When the bromination products of the styryl ligands of formula $[PtBr_4L]_2$, (*9*c) and (*9*d), are refluxed in methanol, colourless monomeric complexes, formulated as $PtBr_2(CH_3OCH{=}CH\text{-}C_6H_4\text{-}AsMe_2)$ and $PtBr_2(CH_3OCH{=}CH\text{-}C_6H_4\text{-}PPh_2)$, and formed according to equation (1), are obtained. From nmr and IR spectroscopic evidence these appear to be the platinum chelate complexes in which a β-proton has been replaced by a methoxy group to give (*10*).

$$\{PtBr_3[\text{-}CH(CH_2Br)\text{-}C_6H_4\text{-}L\text{-}o]\}_2 + 2CH_3OH \longrightarrow 2PtBr_2(CH_3OCH{=}CH\text{-}C_6H_4\text{-}L\text{-}o) + 4HBr \quad \ldots\ldots \quad (1)$$

(L = $AsMe_2$, PPh_2)



(*10*) (c) L = $AsMe_2$

(d) L = PPh_2

Attempts to prepare other alkoxy derivatives of the arsine complex $[PtBr_4(SA)]_2$ only result in the formation of the chelate $PtBr_2(SA)$, whereas the phosphine complex $[PtBr_4(SP)]_2$ will give the corresponding ethoxy derivative, together with the parent chelate complex

$PtBr_2(SP)$, although other alcohols lead to decomposition.

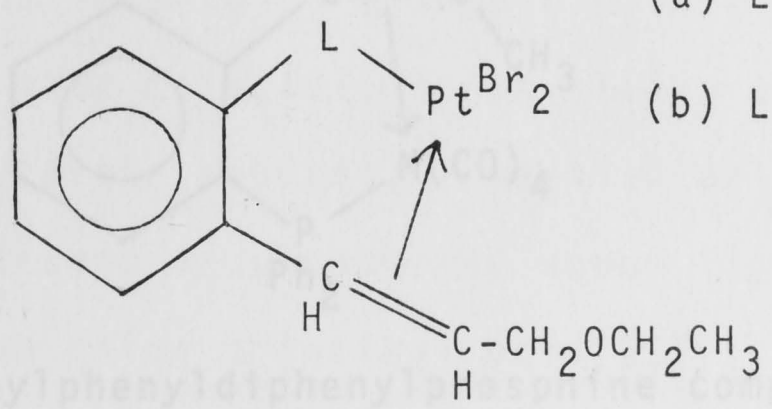
This difference in behaviour is possibly related to the fact that tertiary phosphine complexes are generally more stable than tertiary arsine complexes, for which some evidence can be found in the appreciably lower value of $\nu(C=C)$ in $PtBr_2$ $(SPOCH_3)$, $(1495\ cm^{-1})$ compared with that in $PtBr_2(SAOCH_3)$, $(1518\ cm^{-1})$.[34,37]

The bromination products of the complexes of the allyl ligands (*9*), where L = AA,AP, both react in refluxing ethanol to give similar products. The nmr spectra show that the olefinic side chain has rearranged to give a propenyl derivative, a proton shift having occurred from carbon I to carbon 3 as shown in (*11*).

(a) L = PPh_2

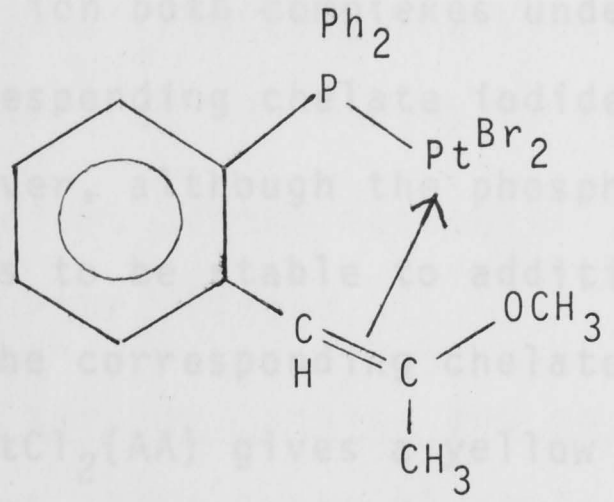
(b) L = $AsMe_2$

(*11*)



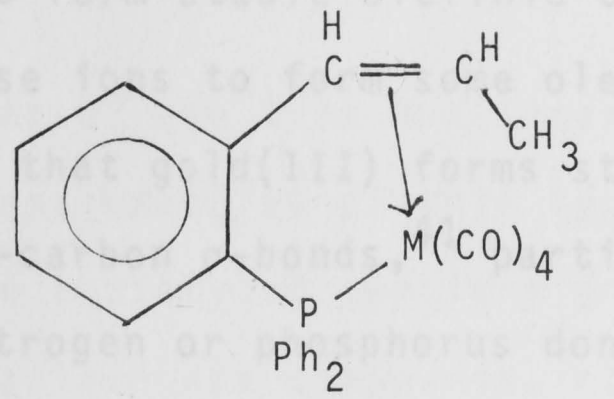
The arsine complex $[PtBr_4(AA)]_2$ (*9*b) also gives similar alkoxy derivatives with methanol, n-propanol, *iso*-propanol and n-pentyl alcohol.

The phosphine complex (*9*a) reacts with methanol but a different alkoxy derivative is obtained. Rearrangement to the propenyl group has again occurred, but this time the β-proton, and not the γ-proton, has been replaced to give (*10*a).



(*10*a)

This isomerisation in the side chain has also been reported[33] in the preparation of Group VI carbonyls containing an olefinic phosphine ligand AP. When an attempt was made to prepare the complex $M(AP)(CO)_4$, where M = Cr,Mo,W, it was found that the ligand had isomerised to the *cis*-propenylphenyldiphenylphosphine



cis o-propenylphenyldiphenylphosphine complex.

From this work it appears that, apart from differences due to stereochemistry, as in the bromination of $PtBr_2(AA)_2$, the phosphines are better chelating agents than the arsines.

Kneen obtained further evidence of this by studying the reaction of the chelate complexes $PtCl_2(AA)$ and $PtCl_2(AP)$ with iodide ion and thiocyanate ion.[40]

With iodide ion both complexes undergo substitution to give the corresponding chelate iodides $PtI_2(AA)$ and $PtI_2(AP)$. However, although the phosphine complex $PtCl_2(AP)$ appears to be stable to addition of thiocyanate ion, and gives the corresponding chelate $Pt(SCN)_2(AP)$, the arsine complex $PtCl_2(AA)$ gives a yellow complex of formula $Pt(NCS)_2(AA)_2$. In this the double bonds of the ligands are uncoordinated, as in the PtX_2L_2 complexes, and the thiocyanate group is N-bonded.

(B) Gold olefinic tertiary phosphine and arsine complexes

Since gold(I) and gold(III) have similar electronic configurations to silver(I) and platinum(II), two metals that are known to form stable olefinic complexes, one would expect these ions to form some olefinic complexes. Also it is known that gold(III) forms stable compounds containing metal-carbon σ-bonds,[41] particularly in the presence of a nitrogen or phosphorus donor ligand,[2] *e.g.* trimethyl phosphine trimethyl gold(III)$(CH_3)_3PAu(CH_3)_3$. Therefore it was decided to use the olefinic phosphines and arsines AP, SP, MP and AA as ligands to see if gold olefinic complexes could be made, and then to study their bromination and see if gold-carbon σ-bonded species of gold(III) could be obtained, similar to the platinum(IV) species obtained on bromination. These four coordinated gold(III) complexes would probably be more soluble and simpler to study than the six coordinated platinum(IV) complexes. From this work Kneen hoped to solve two

outstanding problems from Long and Erskine's work:-

(a) the structure of the compounds $PtBr_4(ligand)_2$

(b) the mechanisms of the ethanolysis of the compounds $PtBr_4(ligand)_2$.

(i) Gold(I) tertiary arsine and phosphine complexes

Gold(I) forms three types of compounds with tertiary arsines and phosphines in which the ligand is monodentate, being coordinated to the gold through the Group V atom. They are classified according to the number of ligand molecules per gold atom as follows:-

(a) $AuX(ligand)$ (b) $AuX(ligand)_2$ (c) $Aux(ligand)_3$

(X = Cl, Br, I).

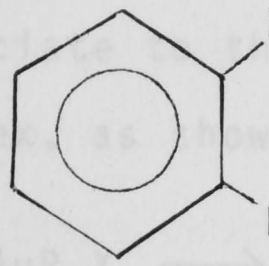
(a) Complexes of the type AuX(ligand).

There are many examples of this type of compound containing a wide variety of tertiary phosphines.[42] They are stable colourless compounds, non-conducting and monomeric in organic solvents, in which the ligands are linearly coordinated about the gold atom, as for example in methyltriphenylphosphine gold, CH_3AuPPh_3.[43]

$$H_3C \text{———} Au \text{———} PPh_3$$

Kneen prepared the gold(I) complexes Au(halogen)(ligand), (*12*,*13*) where L = AP, SP, MP or AA, by the addition of one mole of the complex ion $Au(halide)_2^-$ to one mole of the ligand in ethanol, containing excess lithium halide. The IR spectra of the colourless

crystalline complexes show a band at *ca* 1640 cm^{-1} characteristic of an uncoordinated carbon-carbon double bond.[36] These are therefore formulated as linear gold(I) complexes in which the double bond of the ligand is not coordinated to the metal, as shown below.

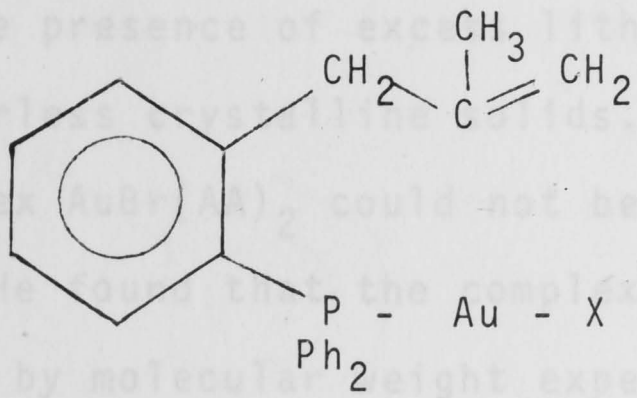


(a) AuX(AP), R = CH_2-CH=CH_2, L = PPh_2

(b) AuX(AA), R = CH_2-CH=CH_2, L = $AsMe_2$

(c) AuX(SP), R = CH=CH_2, L = PPh_2

(*12*) X = Br (*13*) X = Cl.



(e) AuX(MP)

(b) Complexes of the type AuX(ligand)$_2$

Not many examples of this type of compound have been prepared. Those that have are thought to be ionic compounds, containing the linear $(AuL_2)^+$ cation. For example, a preliminary X-ray analysis of the 2-phenyl *iso*-phosphindoline complex Au(*o*-$C_6H_4(CH_2)_2PPh_2)_2I$,[44] shows that the P-Au-P atoms are nearly linear. Some evidence has been quoted for the existence of the three

coordinate complex ion in solution. Westland[45] carried out detailed studies on the conductivity of a nitrobenzene solution of $AuCl(PPh_3)_2$ in the presence of excess ligand, and showed by kinetic studies that the solution contained the undissociated complex $AuCl(PPh_3)_2$. Meyer and Allred[46] had previously reported that its solutions were non-conducting, but explained this by saying that it must dissociate to the phosphine and the linear two coordinated complex, as shown:-

$$AuP_2X \rightleftharpoons P + AuXP \qquad (P = \text{Phosphine})$$

Kneen prepared the phosphine complexes $AuBrL_2$ (*14*), where L = SP, AP, MP, by the addition of two moles of the ligand to one mole of the complex ion $AuBr_2^-$ in ethanol, in the presence of excess lithium bromide, and obtained colourless crystalline solids. The corresponding arsine complex $AuBr(AA)_2$ could not be prepared.

He found that the complexes dissociate in solution as shown by molecular weight experiments. These solutions, even in polar solvents such as nitrobenzene, are non-conducting, and IR and nmr studies show that the double bond is uncoordinated in the solid, as well as in solution.

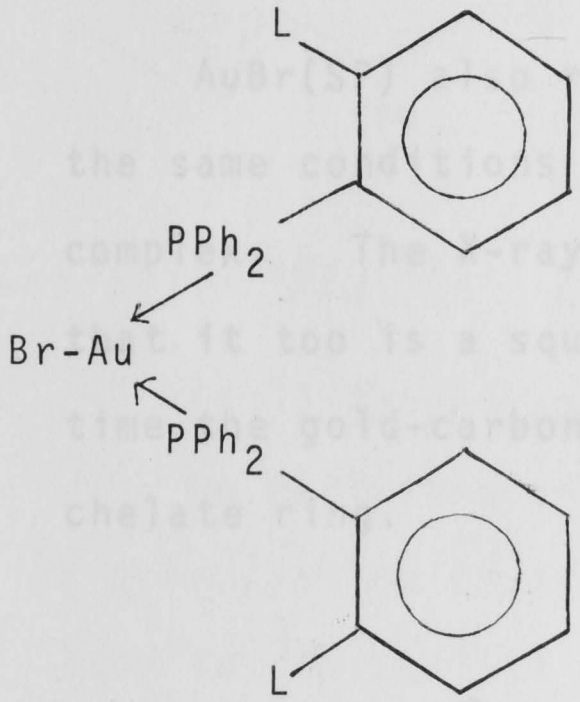
There are therefore two possible ways of explaining these results:-

(a) In the solid state the complexes may exist as ionic species containing the linearly coordinated gold(I) ion $[Au(ligand)_2]^+Br^-$. In solution this changes

to the three coordinated complex $AuBr(ligand)_2$, which dissociates to the linear complex AuBr(ligand) and free ligand, *i.e.*,

$$[Au(ligand)_2]^+Br^- \xrightarrow{\text{solution}} AuBr(ligand)_2 \rightleftharpoons AuBr(ligand) + ligand$$

(b) The complexes may be the first reported examples of three coordinated gold compounds in the solid state, which dissociate in solution as above. If trigonal, these compounds would have the following structures:-



(a) $AuBr(AP)_2$ L = CH_2-CH=CH_2

(d) $AuBr(SP)_2$ L = CH=CH_2

(e) $AuBr(MP)_2$ L = CH_2-C(CH_3)=CH_2

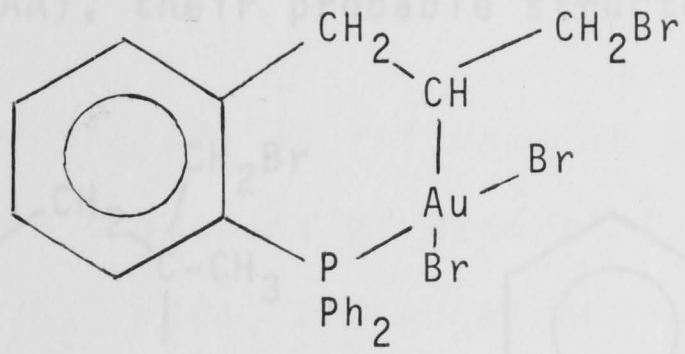
(*14*)

(c) Compounds of the type $AuX(ligand)_3$

Few well characterised compounds of this type have been described.[47] Mann *et al.*[44] have prepared the compounds $AuXP_3$ (X = Cl, Br, I; P = 2-phenyl*iso*-phosphindoline) and these are presumably tetrahedral gold(I) compounds. They are soluble in organic solvents, non-conducting in nitrobenzene, and monomeric in dichloromethane.

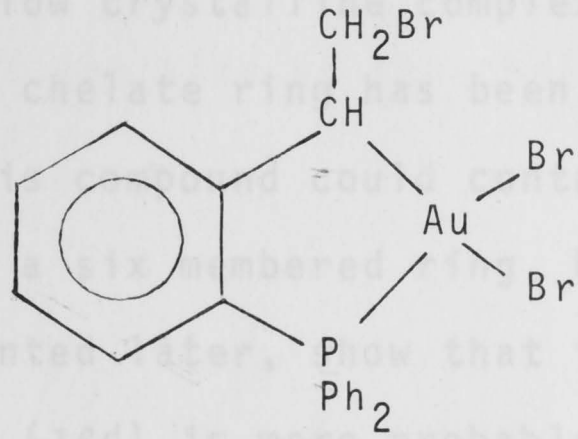
(ii) Bromination of compounds of the type AuBr(ligand)

The complex AuBr(AP) reacts with one mole of bromine in benzene to give a stable deep yellow crystalline complex, shown by X-ray analysis[39] to be a square planar gold(III) complex containing a gold-carbon σ-bond in a six membered chelate ring, as shown below.



(15a) $AuBr_3(AP)$

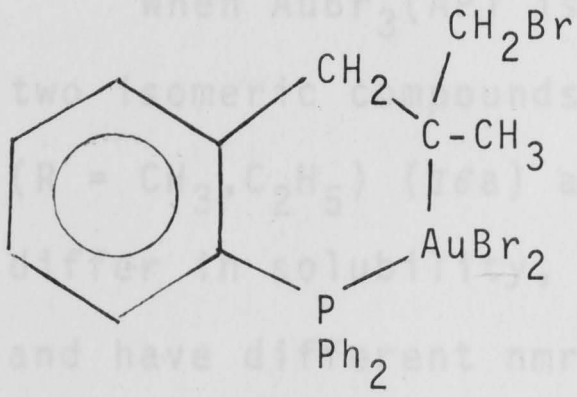
AuBr(SP) also reacts with one mole of bromine under the same conditions to form a stable yellow crystalline complex. The X-ray analysis[39] of this compound shows that it too is a square planar gold(III) complex, this time the gold-carbon σ-bond being in a five membered chelate ring.



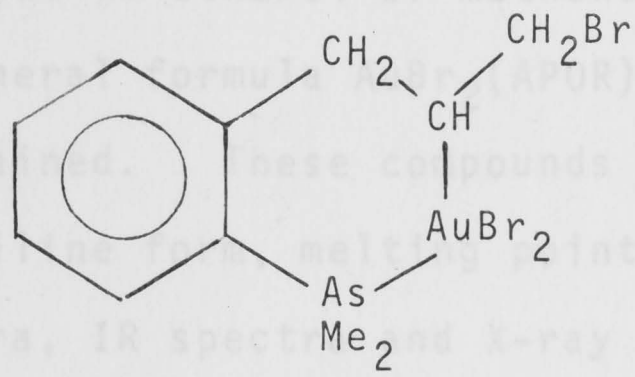
(15d) $AuBr_3(SP)$

Both compounds contain a metal-carbon σ-bond with the unusual grouping RR'CH-Au. Compounds containing metal-carbon σ-bonds usually contain the group $R\text{-}CH_2\text{-}metal$.

On addition of one mole of bromine in benzene the gold(I) complexes AuBr(MP) and AuBr(AA) form unstable complexes, the phosphine complex being deep yellow and the arsine complex a red-brown. By comparison with the more stable products of AuBr(SP) and AuBr(AP), these bromination products are assigned the formulae $AuBr_3$(MP) and $AuBr_3$(AA), their probable structures being given below.



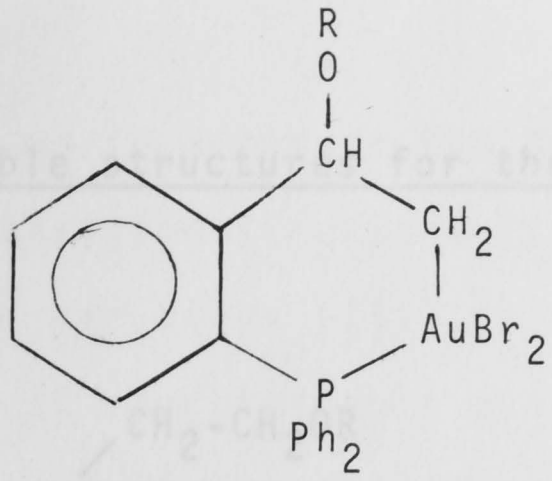
(*15*e) $AuBr_3$(MP)



(*15*c) $AuBr_3$(SA)

(iii) Alcoholysis of compounds of the type $AuBr_3L$

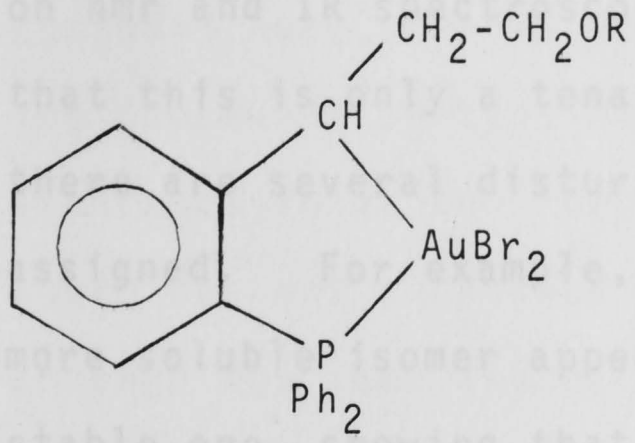
On refluxing in ethanol or methanol, $AuBr_3$(SP) gives a green/yellow crystalline complex in which the bromine atom in the chelate ring has been replaced by an alkoxy group. This compound could contain either a five membered or a six membered ring, but nmr and other evidence to be presented later, show that the six membered chelate ring, as in (*16*d) is more probable.



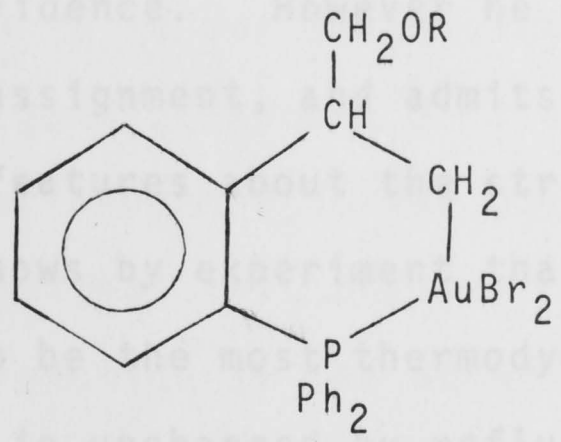
(*16*d) R = CH_3,C_2H_5.

When $AuBr_3$(AP) is refluxed in ethanol or methanol, two isomeric compounds of general formula $AuBr_2$(APOR) (R = CH_3,C_2H_5) (*16*a) are obtained. These compounds differ in solubility, crystalline form, melting point, and have different nmr spectra, IR spectra and X-ray powder photographs. They are both gold(III) square planar complexes containing a gold-carbon σ-bond in a chelate ring, derived from the bromide by replacing the bromine in the chelate ring by an alkoxy group. However they could be two of six possible isomers, depending on the size of the chelate ring, as shown on page 35.

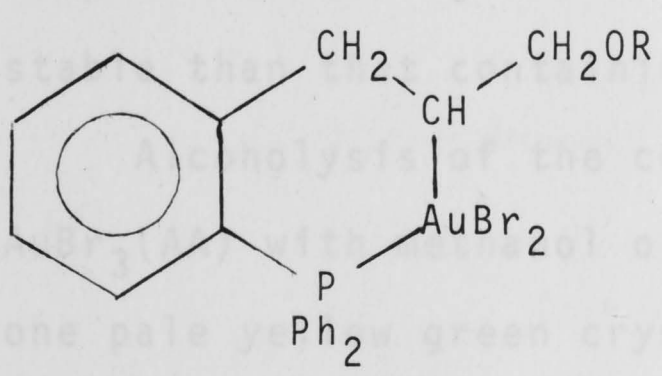
Possible structures for the complex $AuBr_2(APOR)$



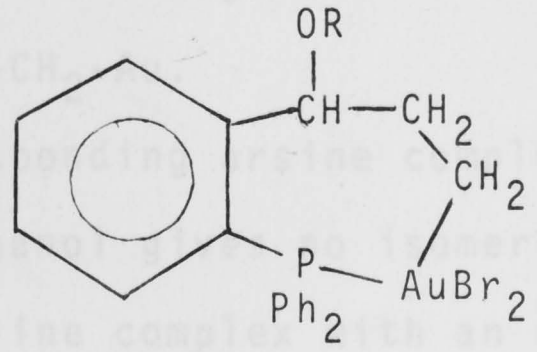
(I)



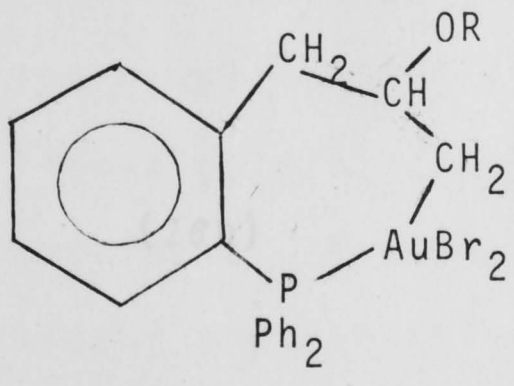
(II)



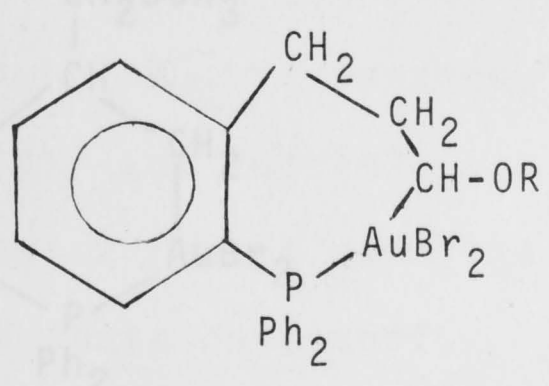
(III)



(IV)



(V)



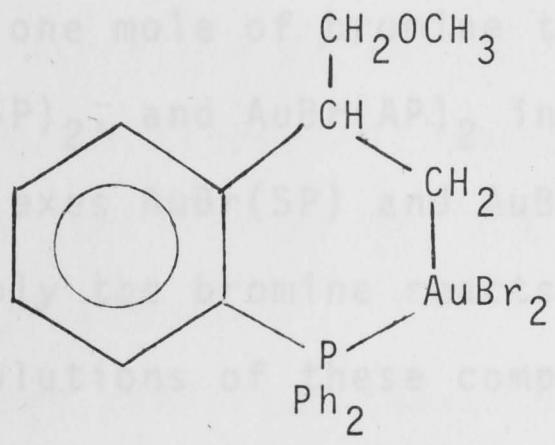
(VI)

R = CH_3, C_2H_5.

Kneen managed to separate the two isomers by recrystallisation and assigned structure (II) to the less soluble prisms, and structure (III) to the more soluble needles, on nmr and IR spectroscopic evidence. However he does say that this is only a tenative assignment, and admits that there are several disturbing features about the structures assigned. For example, he shows by experiment that the more soluble isomer appears to be the most thermodynamically stable one, showing that this is unchanged by refluxing in ethanol, whereas the less soluble one eventually gives a mixture of both isomers. This means that contrary to most previous work on metal-carbon σ-bonded species, the complex containing the RR'-CH-Au arrangement is more stable than that containing R-CH_2-Au.

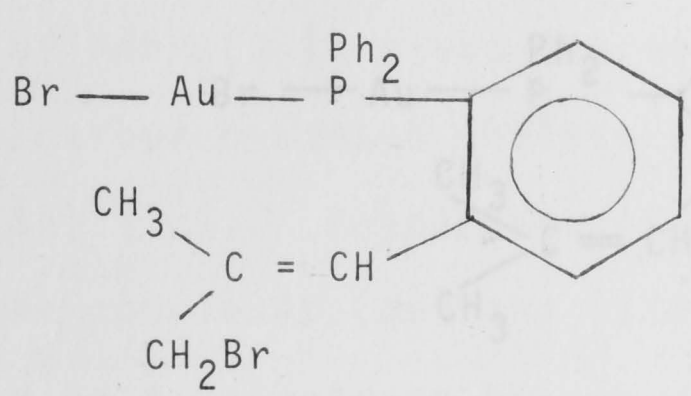
Alcoholysis of the corresponding arsine complex $AuBr_3(AA)$ with methanol or ethanol gives no isomers, only one pale yellow green crystalline complex with an nmr spectrum similar to that of the less soluble isomer of $AuBr_2(APOCH_3)$. Kneen therefore assigned structure (*16*b) to this compound.

(*16*b)



When the complex $AuBr_3(MP)$ is refluxed in ethanol or methanol, HBr is eliminated and a colourless crystalline solid of formula $AuBr_2(MP)$ is obtained. Since the compound $AuBr_3(MP)$ is expected to be the least stable of the compounds of type $AuBr_3(ligand)$, because of steric hindrance about the carbon atom σ-bonded to the gold, Kneen was not surprised to find that this complex did not undergo the same alcoholysis reaction as the other compounds of the same type. He formulated the alcoholysis product as $AuBr_2(MP)$, with the structure shown below, noting that the grouping $CH_3(CH_2Br)C-$ is preserved as postulated in the structure of $AuBr_3(MP)$

(17)



(iv) Bromination of complexes of the type Au(halogen)(ligand)$_2$.

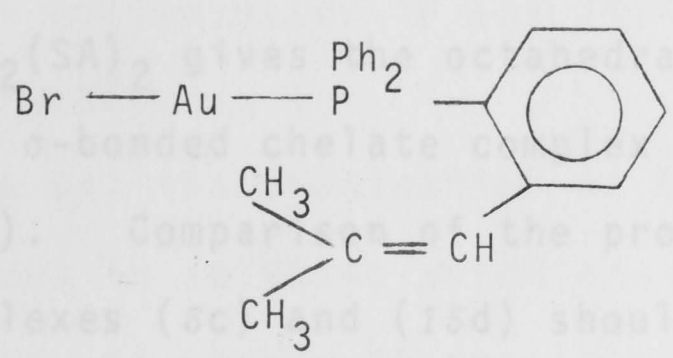
On addition of one mole of bromine to solutions of the complexes $AuBr(SP)_2$, and $AuBr(AP)_2$ in benzene, the linear gold(I) complexes AuBr(SP) and AuBr(AP) are obtained. Presumably the bromine reacts with the free ligand present in solutions of these compounds.

e.g. $AuBr(AP)_2 \rightleftharpoons AuBr(AP) + AP \xrightarrow{Br_2} APBr_2$

The brominated ligands are readily hydrolysed to phosphine oxides and this probably explains why they could not be isolated from the mother liquor.

$AuBr(MP)_2$ reacts with one mole of bromine to give a colourless crystalline complex that from IR and nmr spectroscopic evidence appears to be a linear gold(I) complex of the isomerised ligand *o*-(β-β'-dimethylstyryl)diphenylphosphine.

(*18*)



This isomerisation involving the shift of the double bond, also occurs during the alcoholysis of the bromide $AuBr_3(MP)$, and in the alcoholysis of the allyl dimeric $[PtBr_4L]_2$ complexes, where L = AA and AP. In this case it seems strange that the isomerisation should occur for complexes of the allyl derivative MP, but not for complexes of the allyl ligand AP.

In his work, Kneen therefore succeeded in preparing gold(I) olefinic compounds and showed that these were stable monodentate complexes when the olefinic ligand was

bonded through a phosphorus or arsenic atom. From these he prepared stable organometallic compounds containing a gold-carbon σ-bond in a chelate ring, with properties similar to the corresponding platinum(IV) complexes $PtBr_4(ligand)_2$.

3. Problems arising from the work on gold and platinum olefinic tertiary phosphine and arsine complexes

(i) Bromination of the complex AuBr(SP) gives the gold-carbon σ-bonded chelate complex $AuBr_3(SP)$, in which X-ray crystallographic studies have shown that the gold-carbon σ-bond is formed at the α-carbon atom of the side chain giving a five membered chelate ring (*15*d). Bromination of $PtBr_2(SA)_2$ gives the octahedral platinum(IV)-carbon σ-bonded chelate complex $PtBr_3(SABr)(SA)$ (*3*c). Comparison of the proton nmr spectra of the complexes (*3*c) and (*15*d) should enable a decision to be made between the three possible structures postulated for (*3*c) shown on page 17.

Alcoholysis of $PtBr_3(SABr)(SA)$ gives $PtBr_3(SAOEt)(SA)$ (*6*c), in which, according to X-ray crystallographic studies, the platinum-carbon σ-bond is formed at the β-carbon of the side chain giving a six membered chelate ring. Likewise alcoholysis of $AuBr_3(SP)$ (*15*d) gives $AuBr_2(SPOR)$ (*16*d). Comparison of the proton nmr spectra of (*6*c) and (*16*d) should enable one to decide whether the gold complex (*16*d) also possesses a six membered chelate ring.

Therefore by correlating the nmr spectra with structures of key compounds determined by X-ray crystallography, it should be possible to decide whether bromination and alcoholysis follow essentially similar courses in the platinum and gold series of complexes.

(ii) The isomeric compounds $AuBr_2$(APOR) (*16*a) can have the various different structures shown on page 35. Using nmr spectra and other evidence, it should be possible to decide which of the two structures are most likely for the two isomers.

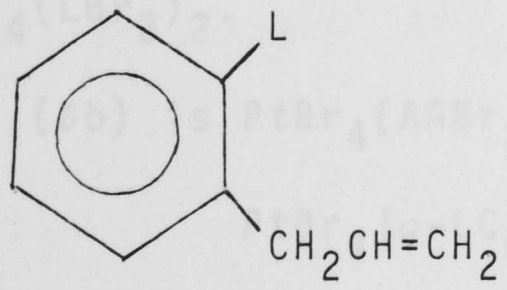
(iii) It has been shown that the bromine atom in the chelate ring in $AuBr_3$(L) (*15*) can be replaced by OR^-, where R = CH_3,C_2H_5. It would be interesting to see if it could be replaced by other nucleophiles in any of the phosphine complexes, *e.g.* $AuBr_3$(SP).

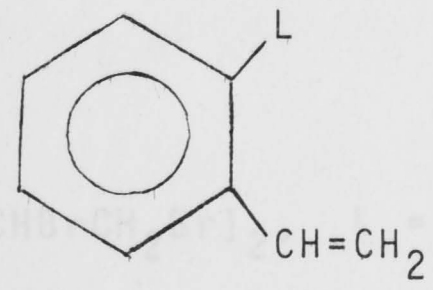
(iv) By carrying out the bromination of the gold(I) and platinum(II) complexes in solvents which are themselves nucleophilic reagents, it should be possible to see if there is any competition between these nucleophiles and Br^- during bromination, and this could help to elucidate the mechanisms involved.

(v) It would be interesting to see if the corresponding gold(I) and platinum(II) chloro complexes could be prepared, and if chlorination of these complexes proceeded similarly to bromination.

4. <u>Numbering system for the gold and platinum olefinic tertiary phosphine and arsine complexes in Chapter I</u>.

(*1*) Ligand



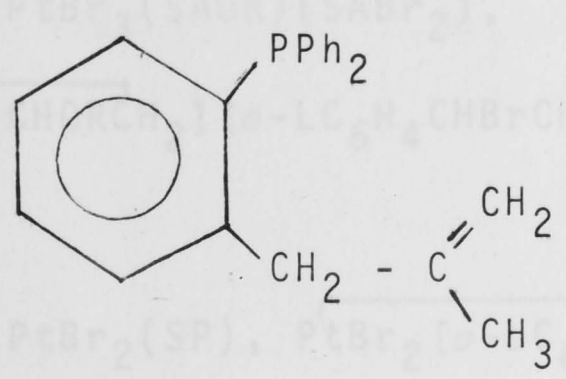


(a) L = PPh_2(AP)

(b) L = $AsMe_2$(AA)

(c) L = $AsMe_2$(SA)

(d) L = PPh_2(SP)



(e) MP

<u>Platinum Complexes</u> ..... in all complexes L = ligand.

(*2*) $PtBr_2(L)_2$.

e.g. (*2*a) is $PtBr_2(AP)_2$, $PtBr_2[o\text{-}LC_6H_4CH_2CH{=}CH_2]_2$,

L = PPh_2.

(*3*) $PtBr_3(LBr)(L)$.

e.g. (*3*c) is $PtBr_3(SABr)(SA)$,

$PtBr_3[o\text{-}LC_6H_4CH(CH_2Br)][o\text{-}LC_6H_4CH{=}CH_2]$, L = $AsMe_2$.

(*4*) $PtBr_3(LBr)(LBr_2)$.

e.g. (*4*c) is $PtBr_3(SABr)(SABr_2)$,

$P\overline{tBr_3[o\text{-}LC_6H_4CH(CH_2Br)]}[o\text{-}LC_6H_4CHBrCH_2Br]$, L = $AsMe_2$.

(*5*) $PtBr_4(LBr_2)_2$.

e.g. (*5*b) is $PtBr_4(AABr_2)_2$,

$PtBr_4[o\text{-}LC_6H_4CH_2CHBrCH_2Br]_2$, L = $AsMe_2$.

(*6*) $PtBr_3(LOR)(L)$.

e.g. (*6*c) is $PtBr_3(SAOR)(SA)$,

$P\overline{tBr_3[o\text{-}LC_6H_4CHORCH_2}][o\text{-}LC_6H_4CH{=}CH_2]$, L = $AsMe_2$.

(*7*) $PtBr_3(LOR)LBr_2)$.

e.g. (*7*c) is $PtBr_3(SAOR)(SABr_2)$,

$P\overline{tBr_3[o\text{-}LC_6H_4CHORCH_2}][o\text{-}LC_6H_4CHBrCH_2Br]$, L = $AsMe_2$.

(*8*) $PtBr_2(L)$.

e.g. (*8*d) is $PtBr_2(SP)$, $P\overline{tBr_2[o\text{-}LC_6H_4CH{=}CH_2]}$, L = PPh_2.

(*9*) $[PtBr_3(LBr)]_2$

e.g. (*9*d) is $[PtBr_3(SPBr)]_2$,

$\{P\overline{tBr_3[o\text{-}LC_6H_4CH(CH_2Br)}\text{-}]\}_2$, L = PPh_2.

(*10*) $PtBr_2(LOCH_3)$.

e.g. (*10*d) is $PtBr_2(SPOCH_3)$,

$P\overline{tBr_2[o\text{-}LC_6H_4CH{=}CHOCH_3}]$, L = PPh_2.

(*11*) $PtBr_2\ (LOC_2H_5)$.

e.g. (*11*d) is $PtBr_2(SPOC_2H_5)$,

$P\overline{tBr_2[o\text{-}LC_6H_4CH{=}CHOC_2H_5}]$, L = PPh_2.

Gold Complexes

(*12*) $AuBrL$.

e.g. (*12*d) is $AuBr(SP)$, $AuBr[o\text{-}LC_6H_4CH{=}CH_2]$, L = PPh_2.

(*13*) $AuClL$.

e.g. (*13*a) is $AuCl(AP)$, $AuCl[o\text{-}LC_6H_4CH_2CH{=}CH_2]$,

L = PPh_2.

(*14*) $AuBrL_2$.

e.g. (*14*d) is $AuBr(SP)_2$.

(*15*) $AuBr_3L$.

e.g. (*15*d) is $AuBr_3(SP)$, $AuBr_3[o\text{-}LC_6H_4CH(CH_2Br)]$,

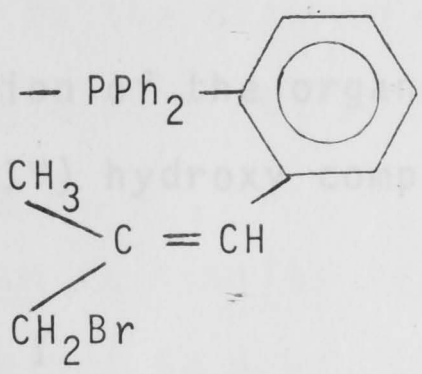
L = PPh_2.

(*16*) $AuBr_2(LOR)$.

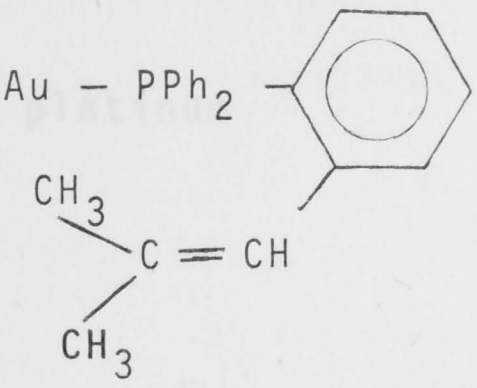
e.g. (*16*d) is $AuBr_2(SPOR)$, $AuBr_2[o\text{-}LC_6H_4CHORCH_2]$,

L = PPh_2.

(*17*)



(*18*)



CHAPTER II

Organometallic gold(III) and platinum(IV) bromo compounds derived from *o*-styryldimethylarsine and *o*-styryldiphenylphosphine.

A. Nmr spectra of the chelate ring protons.

B. Preparation of the organometallic gold(III) complex derived from *o*-styryldiphenylphosphine.

C. Preparation of the organometallic platinum(IV) complex derived from *o*-styryldimethylarsine.

D. Attempted preparation of the organometallic gold(III) complex derived from *o*-styryldimethylarsine.

E. Reactions of the organometallic platinum(IV) complex.

F. Reactions of the organometallic gold(III) complex.

G. The reaction of the organometallic gold(III) and platinum(IV) hydroxy complexes with hydrogen bromide.

Nmr Table I.

Numbering system for the gold and platinum complexes in Chapter II.

Organometallic gold(III) and platinum(IV) bromo compounds derived from *o*-styryldimethylarsine and *o*-styryldiphenylphosphine.

A. Nmr spectra of the chelate ring protons

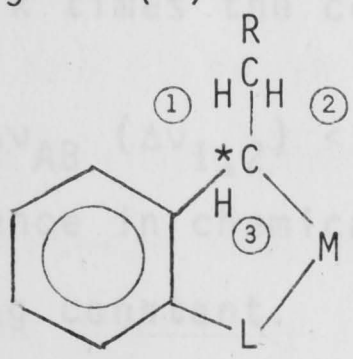
This chapter describes the preparation and reaction of various organometallic complexes containing five or six membered chelate rings. Where an X-ray crystal structure determination has not been carried out the size of the chelate ring is determined from the nmr spectra of the complex. Therefore it is intended to review briefly first the different chelate ring proton nmr spectra associated with the complexes, and show how these are used to indicate the size of the chelate ring.

The pattern of the resonances due to the chelate ring protons in these complexes always approximates to one of the three shown in the diagram on page 48. Each pattern will be dealt with separately.

(a) Pattern A.

This diagram is similar to the nmr spectrum of the chelate ring protons in $AuBr_3$ (SP) (*15*d) which has been shown by X-ray crystallography to contain a five membered chelate ring.[39] (I)

(I)

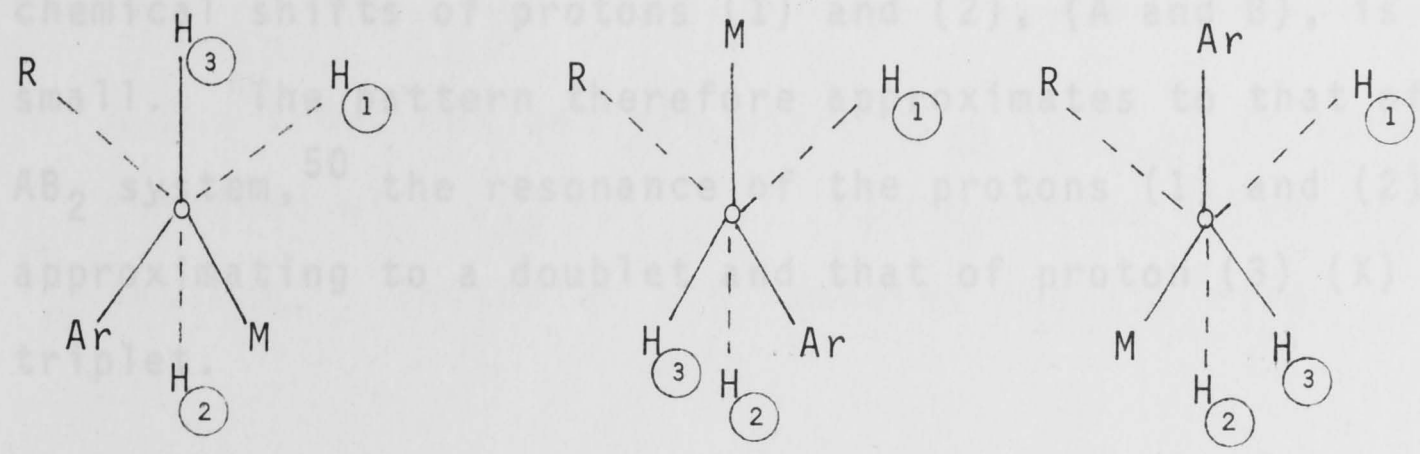


L = $AsMe_2$, PPh_2.

M = Au, Pt.

R = Br, Cl, OCH_3, OC_2H_5, $OCOCH_3$, OH.

In this type of complex protons (1) and (2) are on a carbon atom which is itself attached to an asymmetric carbon atom (*C); therefore, even if freely rotating, these protons are never equivalent and have different chemical shifts.[48]



o = Axis of C-C bond.

Generally three protons having different chemical shifts would constitute an ABC system. However in this case the difference between the chemical shift of proton (3), and that of either proton (1) or proton (2), is so large compared with the difference in chemical shift between protons (1) and (2), that the three protons constitute an ABX system. This is a second order spectrum, the general rule being applied that it becomes higher order because the difference in chemical shift between the A and B nuclei is less than six times the coupling constant between A and B.

i.e. $\Delta\nu_{AB}$ ($\Delta\nu_{1,2}$) < 6 x J_{AB} ($J_{1,2}$)

$\Delta\nu$ = difference in chemical shift.

J = coupling constant.

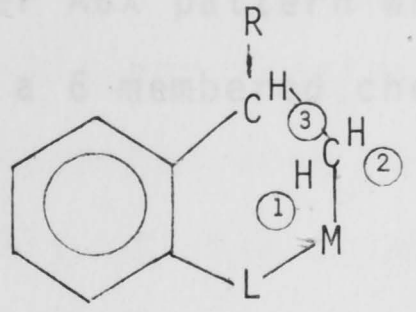
Proton (3) is the X proton of the ABX system.

A typical ABX pattern has a series of eight lines for the combined AB protons' resonance and a quartet for the X proton resonance, except when $\Delta\nu_{AB}$ is very small compared with J_{AB}, as in the proton nmr spectrum of a five membered chelate ring complex. Here the difference between the chemical shifts of protons (1) and (2), (A and B), is very small. The pattern therefore approximates to that of an AB_2 system,[50] the resonance of the protons (1) and (2) approximating to a doublet and that of proton (3) (X) to a triplet.

(b) Pattern B.

This diagram is similar to the pattern obtained for the chelate ring protons in $PtBr_3(SAOEt)(SA)$ (*6*c) which has been shown by X-ray crystallography[3] to contain a six membered chelate ring. (II)

(II)



M = Au, Pt

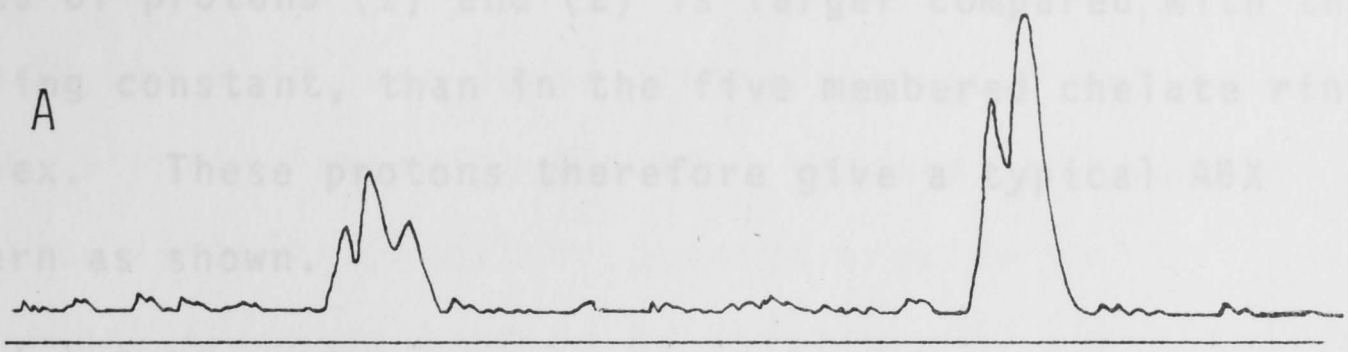
L = $AsMe_2$, PPh_2

R = Cl, Br, OCH_3, OC_2H_5, OH, $OCOCH_3$.

In the six membered chelate ring complex the protons (1) and (2) are fixed in the ring system and therefore each has a different chemical shift. As before, the difference between the chemical shifts of protons (1), (2) and (3) means that they constitute an ABX system.

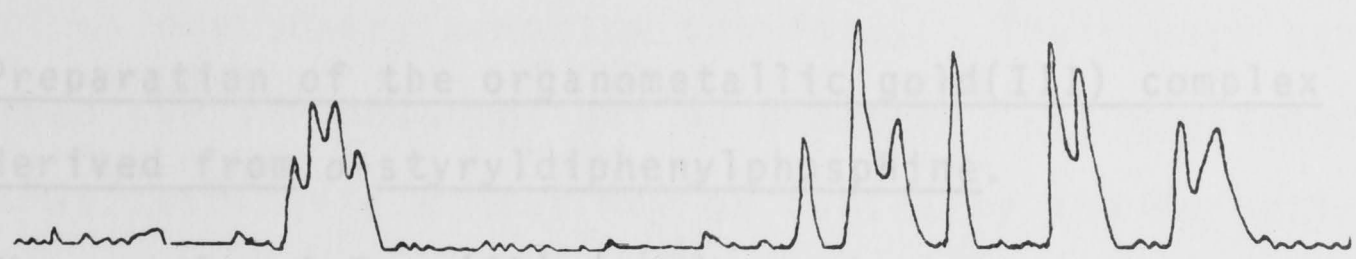
Nmr patterns due to the protons of the chelate ring

A



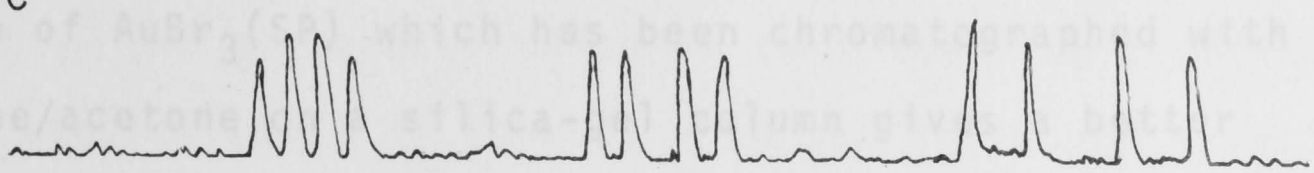
A 2nd order ABX pattern where $\Delta\nu_{AB}$ ($\Delta\nu_{1,2}$) is very small compared with J_{AB} ($J_{1,2}$). Approximates to an AB_2 pattern. Indicates a 5 membered chelate ring.

B



A 2nd order ABX pattern where $\Delta\nu_{AB}$ ($\Delta\nu_{1,2}$) < $6J_{AB}$($J_{1,2}$). Indicates a 6 membered chelate ring.

C



A 1st order AMX pattern where $\Delta\nu_{AB}$ ($\Delta\nu_{1,2}$) > $6J_{AB}$($J_{1,2}$). Indicates a 6 membered chelate ring.

However in this case the difference between the chemical shifts of protons (1) and (2) is larger compared with their coupling constant, than in the five membered chelate ring complex. These protons therefore give a typical ABX pattern as shown.

(c) Pattern C.

If $\Delta\nu_{1,2} \geqslant 6J_{1,2}$ in the six membered chelate ring complex then the system can be treated, to a reasonable approximation, as a first order one. This gives the AMX pattern shown in C which consists of three doublets, each split further into a doublet, making twelve lines altogether.

B. Preparation of the organometallic gold(III) complex derived from *o*-styryldiphenylphosphine.

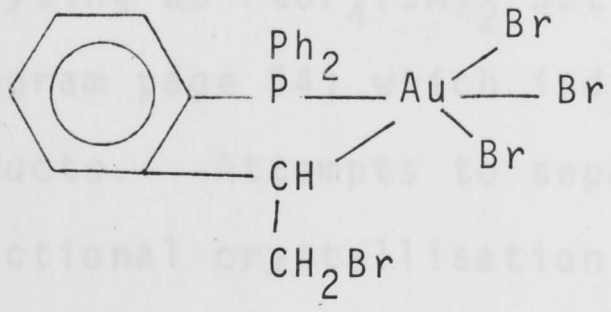
The complex $AuBr_3$ (SP) (*15*d) can be prepared as previously described, by bromination of the gold(I) complex AuBr(SP).[32] All nmr spectra of the complex $AuBr_3$(SP) obtained by Kneen had been poorly resolved as the complex is only slightly soluble in many organic solvents, *e.g.* chloroform, benzene, dichloromethane. However, during an attempt to prepare a derivative, it has been found that a sample of $AuBr_3$(SP) which has been chromatographed with benzene/acetone on a silica-gel column gives a better resolved spectrum. This spectrum is essentially the same as that obtained by Kneen, showing that the complex is chemically unchanged, but is better resolved because the

chromatographed complex appears to be more soluble in organic solvents.

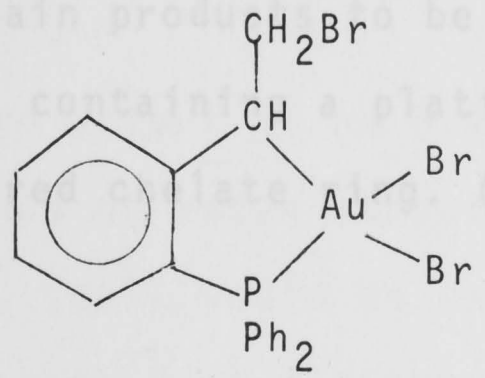
It has also been found that addition of the quaternary salts tetraethylammonium bromide, tetramethylammonium bromide, methyltriphenylphosphonium bromide or tetraphenylarsonium bromide to solutions of $AuBr_3(SP)$ also increases its solubility, enabling better resolved nmr spectrum to be obtained without apparently changing the complex.

A similar phenomenon has been reported by Desnoyers, Pelletier and Jolicoeur[51] who have noted that the solubility of benzene in water is increased in the presence of various quaternary ammonium bromides. Their work has confirmed earlier observations by Diamond[52] who suggested that this salting-in effect may be caused by the formation of an association complex between the large ion and the non-electrolyte, induced by the structure of water. It is noted in the case of the gold(III) complex however that the quaternary salts only seem to increase the solubility of the complex in organic solvents, (*e.g.* chloroform, benzene), no effect being observed in water.

One other explanation for the increase in solubility caused by the quaternary salts is that the five coordinate ionic species (III) is formed, although one would expect to see some change in the colour of the solution due to the increased coordination of the gold atom.

III 

An X-ray structure determination on $AuBr_3(SP)$[39] has shown it to have the structure (*15*d), two bromine atoms, a phosphorus atom and the α-carbon atom of the side chain forming a planar array about the metal, and the five membered chelate ring containing the gold-carbon σ-bond having an envelope conformation.

(*15*d) 

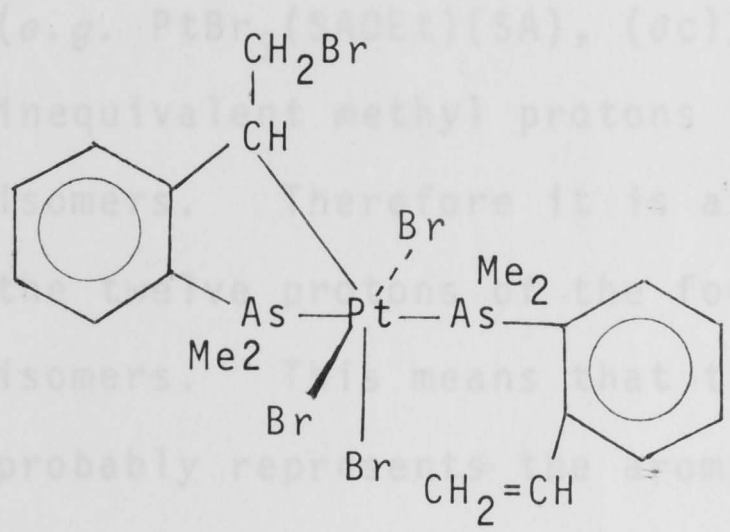
The nmr spectrum of its chelate ring protons (see table I) shows a pattern similar to A (see page 48), the complex at *ca* 5.8τ approximating to a doublet as expected for a five membered chelate ring complex. The ^{31}P decoupled 100-MHz proton nmr spectrum is still too complex to be analysed as an ABX pattern so that accurate values for the chemical shifts cannot be obtained.

C. <u>Preparation of the organometallic platinum(IV) complex derived from *o*-styryldimethylarsine</u>.

The bromination of the platinum(II) bis-complex $PtBr_2(SA)_2$ (*2*c) is carried out as described[4] to give a

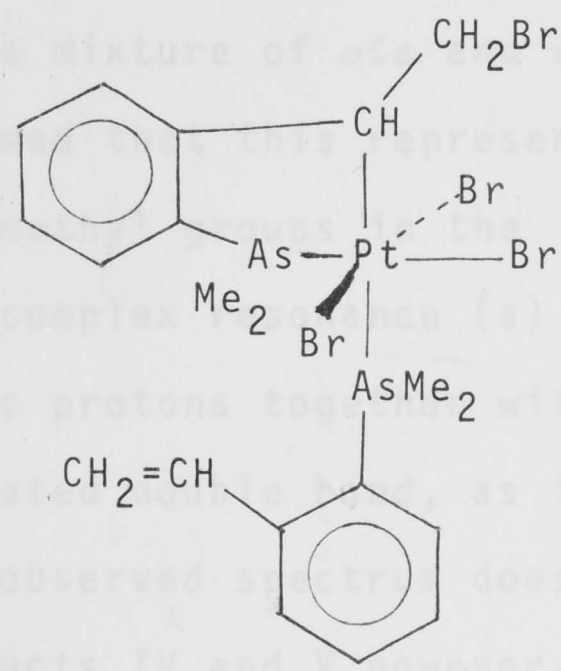
yellow solid analysing as $PtBr_4(SA)_2$ but having an nmr spectrum (see diagram page 54) which indicates that it is a mixture of products. Attempts to separate the components by fractional crystallisation have been unsuccessful; the nmr spectrum of each fraction being identical with that of the original compound. An attempt to purify the compound by chromatography on silica gel or alumina gives a new compound which is described later (see page 66).

By comparison with the bromination of $AuBr_3(SP)$ (*15*d) one would expect the main products to be the *cis* and *trans* platinum(IV) complexes containing a platinum-carbon σ-bond in a five membered chelate ring. (IV and V).



IV

(*trans*)



V

(*cis*)

A mixture of these two complexes would be expected to give one of the following nmr spectra.

(1) $\tau(CDCl_3)$ 2.0 - 3.0 (m,9,Ar + =C*H*-), 4.0 - 5.0 (dd,2, = CH_2), *ca* 8.0 (m, 12, $AsCH_3$), plus resonances due to the chelate ring protons.

(2) $\tau(CDCl_3)$ 2.0 - 3.0 (m,8,Ar), ? (m,1, =C*H*-), 4.0 - 5.0 (dd,2, =CH_2), *ca* 8.0 (m,12, $AsCH_3$), plus resonances due to the chelate ring protons.

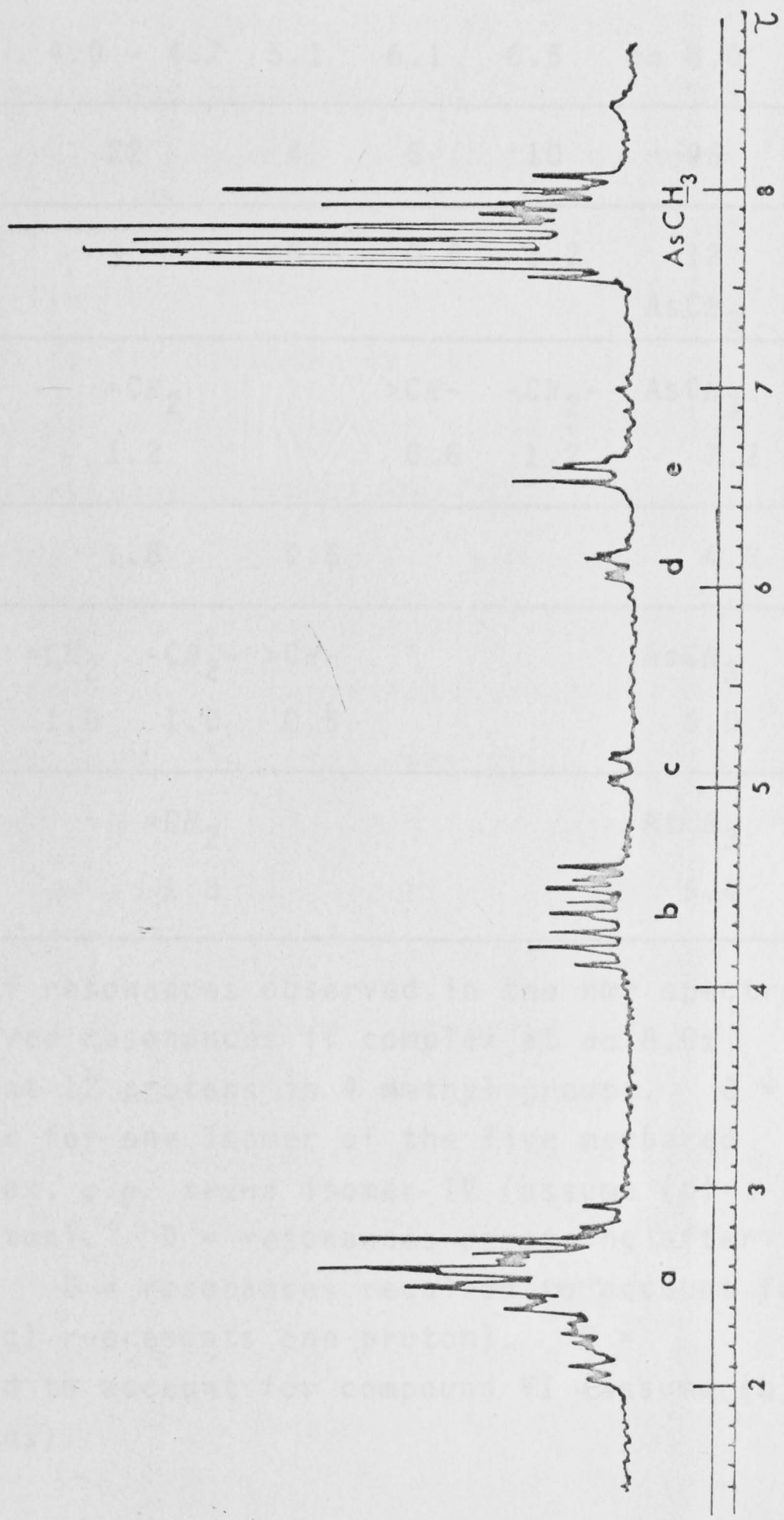
The observed nmr spectrum (see diagram on page 54) shows the following:

$\tau(CDCl_3)$ 2.0 - 3.0 (m,10,a), 4.5 - 5.0 (m,3,b), 5.1 (m,0.5,c), 6.1 (m,0.6,d), 6.5 (m,1.2,e), *ca* 8.0 (m,12, $AsCH_3$).

A very complex resonance occurs at *ca* 8.0τ which by comparison with compounds of known structure (*e.g.* $PtBr_3$(SAOEt)(SA), (*6*c)), would be expected for the inequivalent methyl protons in a mixture of *cis* and *trans* isomers. Therefore it is assumed that this represents the twelve protons of the four methyl groups in the isomers. This means that the complex resonance (a) probably represents the aromatic protons together with the α-vinyl proton of the uncoordinated double bond, as in the postulated spectrum (1). The observed spectrum does not account for the postulated products IV and V however, for the following reasons:-

(a) A complex resonance approximating to eight lines which can be described as two overlapping pairs of doublets (J = 17Hz, 11Hz) is seen in the region 4.5τ - 5.0τ.

Nmr spectrum of the bromination product of $PtBr_2(SA)_2$



Integration of resonances observed in the nmr spectrum of the bromination product of $PtBr_2(SA)_2$.

$\tau(CDCl_3)$

	a	b	c	d	e	f
	2.0 - 3.0	4.0 - 4.7	5.1	6.1	6.5	*ca* 8.0
A	80	22	4	5	10	96
B	10	3	0.5	0.6	1.2	12
						$AsCH_3$
C	Ar =C*H*-	=CH_2		>C*H*-	-CH_2-	$AsCH_3$
	4.8 0.6	1.2		0.6	1.2	7.2
D	4.6	1.8	0.5			4.8
E	Ar =C*H*-	=CH_2	-CH_2-	>C*H*-		$AsCH_3$
	4.0 0.5	1.0	1.0	0.5		6.0
F	Ar =C*H*-	=CH_2				$AsCH_3$
	4.5	1.8				5.4

A = actual ratio of resonances observed in the nmr spectrum. B = ratio of observed resonances if complex at *ca* 8.0τ assumed to represent 12 protons in 4 methyl groups. C = resonances required for one isomer of the five membered chelate ring complex, *e.g. trans* isomer IV (assume (d) represents one proton). D = resonances remaining after accounting for IV. E = resonances required to account for isomer V (assume (c) represents one proton). F = resonances required to account for compound VI (assume (b) represents 4 protons).

The pattern is roughly as expected for a mixture of *cis* and *trans* isomers, since the β-vinyl resonances would be expected to differ in chemical shift, but integration shows that the resonance corresponds to three protons, not two. (b) If it is assumed that the two resonances (d) and (e) represent the chelate ring protons, then these resonances are not intense enough when compared with the resonance due to the methyl protons which is assumed to represent twelve protons. Resonance (d) should integrate as one proton, (e) as two protons. There is also an additional resonance (c) which is difficult to assign.

Three attempts are made to explain these anomalies although no one explanation is completely satisfactory. (1) The chelate ring protons of the *cis* and *trans* isomers could give rise to different resonances, the complex resonances (d) and (e) representing the chelate ring protons in one isomer, say the *trans* one. These resonances approximate to the pattern A (see page 48) and therefore probably represent the protons in a five membered chelate ring. If (e) represents two protons (1.2 units) then part of the complex resonance (b) (1.2 units) represents the two uncoordinated β-vinyl protons in this isomer. The remainder of the resonance (b) (1.8 units) must then represent the other isomer, say the *cis* one. The complex resonance (c) appears to be a pattern typical of the single proton in a chelate ring, therefore this could be due to the single proton

in the chelate ring of the *cis* isomer, being 0.5 units representing one proton. The resonance due to the other two protons of the chelate ring could lie underneath the resonance (b) together with the resonance due to the two uncoordinated β-vinyl protons in this isomer. This would mean that 1.8 units represented four protons. However, as shown in the table on page 55, the observed resonances still do not integrate correctly, the resonances (b) and (f) being too low in intensity for the presence of another isomer.

The following are not accounted for:-

(i) the above supposes that the resonance due to the $-CH_2-$ protons of the chelate ring lies at a lower field than that due to the >CH- proton in one of the isomers, say the *cis* isomer. But in all the related chelate ring complexes studied the reverse is true.

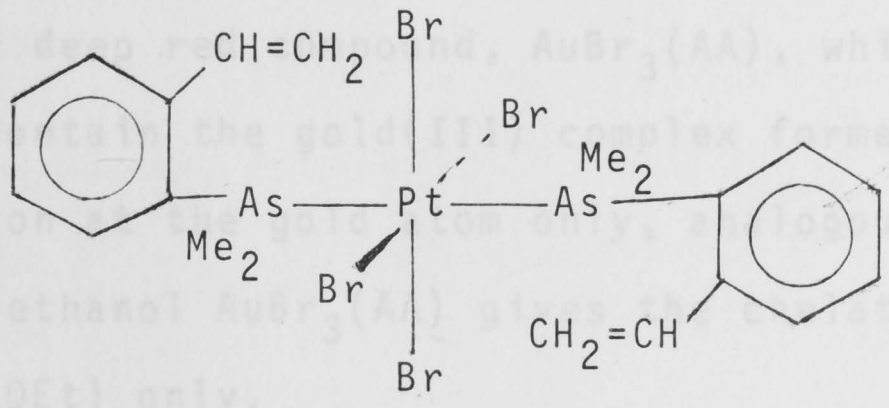
(ii) The resonance due to the methyl protons in the nmr spectrum of the complex $PtBr_2(SA)_2$ (*2*c), shows that it contains a mixture of *cis* and *trans* isomers (see Table I). However the resonance due to the uncoordinated β-vinyl protons in (*2*c) is still only a pair of doublets, not a complex resonance.

(iii) An X-ray crystal structure determination[3] shows that the ethanolysis product $PtBr_3(SAOEt)(SA)$ (*6*c) obtained from (*3*c) has a six membered chelate ring structure and is present as the *trans* isomer only. The nmr spectrum suggests that this isomer is also present in solution.

Molecular models indicate that the steric hindrance present in the *cis* form of (*6*c) is no greater than that in the *cis* form of the five membered chelate ring complex (*3*c). Therefore it is difficult to explain why both isomers should be present in (*3*c), and only one isomer in (*6*c).

(2) The bromination product could be a mixture of one of the five membered chelate ring isomers and a complex VI formed by oxidative-addition at the metal only.

VI



A similar complex is postulated as being formed during the bromination of the AuBr(SP) (Chapter IV) and the attempted preparation of the σ-bonded complex $AuBr_3$(SA). In complex VI the pair of doublets due to uncoordinated β-vinyl protons could be shifted upfield from those in IV or V, thus accounting for the extra peaks observed in the region 4.0τ - 5.0τ (see page 54). However if the bromination product is assumed to be a mixture of IV or V, and also VI, the observed resonances apparently still do not integrate correctly. It is difficult to account for the resonance at 5.1τ and the observed methyl resonance is not intense enough. The additional resonances which could account for the compound VI can only account for ten

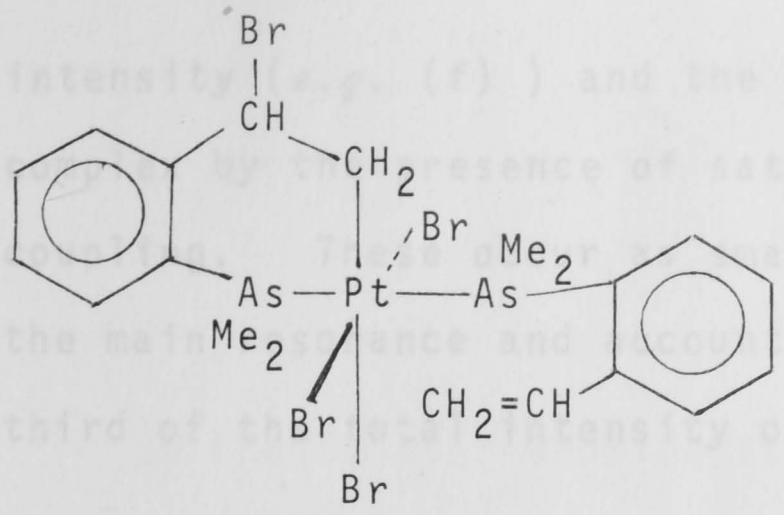
protons at *ca* 8.0τ instead of the twelve protons required for the four methyl groups (see Table on page 55). An X-ray structure determination[3] has shown that only one product, the *trans* $PtBr_3(SAOEt)(SA)$ (*6*c), is obtained when the mixture $PtBr_4(SA)_2$ is refluxed in ethanol. Therefore any postulated component of the mixture must form (*6*c) with ethanol. It is possible that VI would convert (*6*c) in ethanol as a similar reaction appears to take place in the gold series. Kneen[32] found that bromination of AuBr(AA) gives a deep red compound, $AuBr_3(AA)$, which is now thought to contain the gold(III) complex formed by oxidative-addition at the gold atom only, analogous to VI. On refluxing in ethanol $AuBr_3(AA)$ gives the chelate ring complex $AuBr_2(AAOEt)$ only.

However the presence of VI as well as either IV or V still does not account for the observed nmr spectrum.

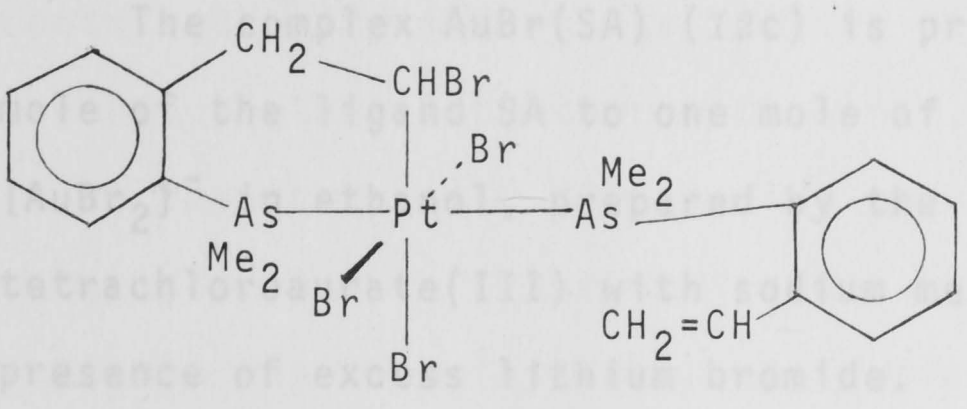
(i) The spectrum does not integrate correctly and the resonance at 5.1τ cannot be accounted for.

(ii) One would expect the methyl protons in either the *cis* or the *trans* isomers of VI to be equivalent , giving rise to singlets (with platinum satellites) as observed in the spectrum of $PtBr_2(SA)_2$ (*2*c). The observed resonance at *ca* 8.0τ is far too complex to allow for the presence of VI and either IV or V only.

(3) The bromination product could contain one of the six membered chelate ring complexes VII or VIII as well as one of the isomers IV or V.



VII



VIII

The complex resonance at 5.1τ could be due to one of the chelate ring protons, resonances due to the other chelate ring protons lying under the resonance (a) or (b). However again it is difficult to make the observed resonances fit the required integration.

Summary

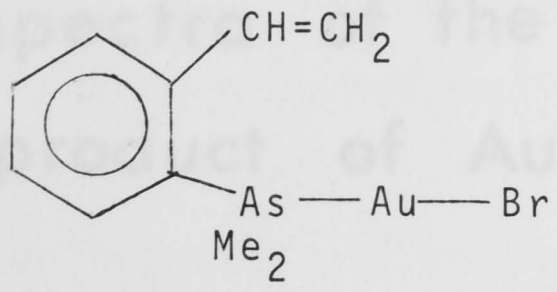
Using the nmr spectrum of the bromination product it has not been possible to decide the exact structure of the components of $PtBr_4(SA)_2$. An attempt has been made to decide on possible products using the integration of the nmr spectrum but this method is not very reliable. Inaccuracies occur when resonances of low intensity (*e.g.* (c), (d) and (e)) are compared with those of high

intensity (*e.g.* (f)) and the problem is also made more complex by the presence of satellites due to ^{195}Pt coupling. These occur as small peaks on either side of the main resonance and account for approximately one third of the total intensity observed.

D. Attempted preparation of the organometallic gold(III) complex derived from *o*-styryldimethylarsine

The complex AuBr(SA) (*12*c) is prepared by adding one mole of the ligand SA to one mole of the complex ion $[AuBr_2]^-$ in ethanol, prepared by the reduction of sodium tetrachloroaurate(III) with sodium metabisulphite in the presence of excess lithium bromide. It is an unstable white crystalline solid which decomposes to a grey solid on attempted recrystallisation. Its nmr spectrum shows a resonance at *ca* 4.5τ which is typical of the β-vinyl protons of an uncoordinated vinyl group (see Table I) while its IR spectrum has bands at 920 cm^{-1} and 980 cm^{-1} due to out-of-plane $=CH_2$ and =CH- deformations.[36] Like several other complexes of the styryl ligands this complex does not show the expected band at *ca* 1640 cm^{-1} due to the free C=C stretching frequency. Presumably this particular band has a very low intensity in derivatives of the styryl ligands. AuBr(SA) is therefore formulated as a linear gold(I) complex (*12*c) containing an uncoordinated double bond in the ligand.

(*12*c)

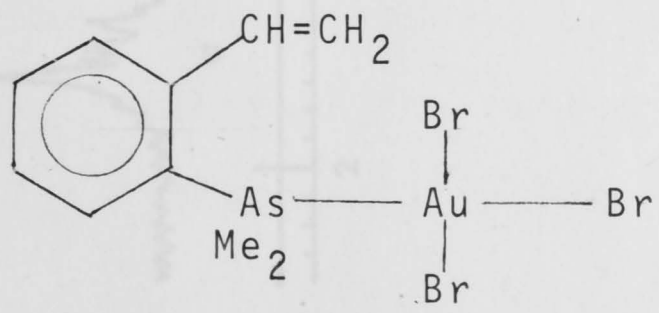


On addition of bromine in benzene to a solution of complex (*12*c) in benzene, a red/brown crystalline solid is precipitated. The nmr spectrum of this solid (see diagram page 63) shows a complex resonance (c) which could contain a pair of doublets typical of the uncoordinated β-vinyl protons, together with other resonances. There is no resonance at 8.15τ showing that no unchanged starting material (*12*c) is present; instead three new singlets, possibly due to methyl protons, appear at lower field.

The IR spectrum of the solid seems to have bands at *ca* 920 cm^{-1} and *ca* 980 cm^{-1} due to out-of-plane deformations,[36] although the quality of the spectrum is poor since the solid will not mull readily.

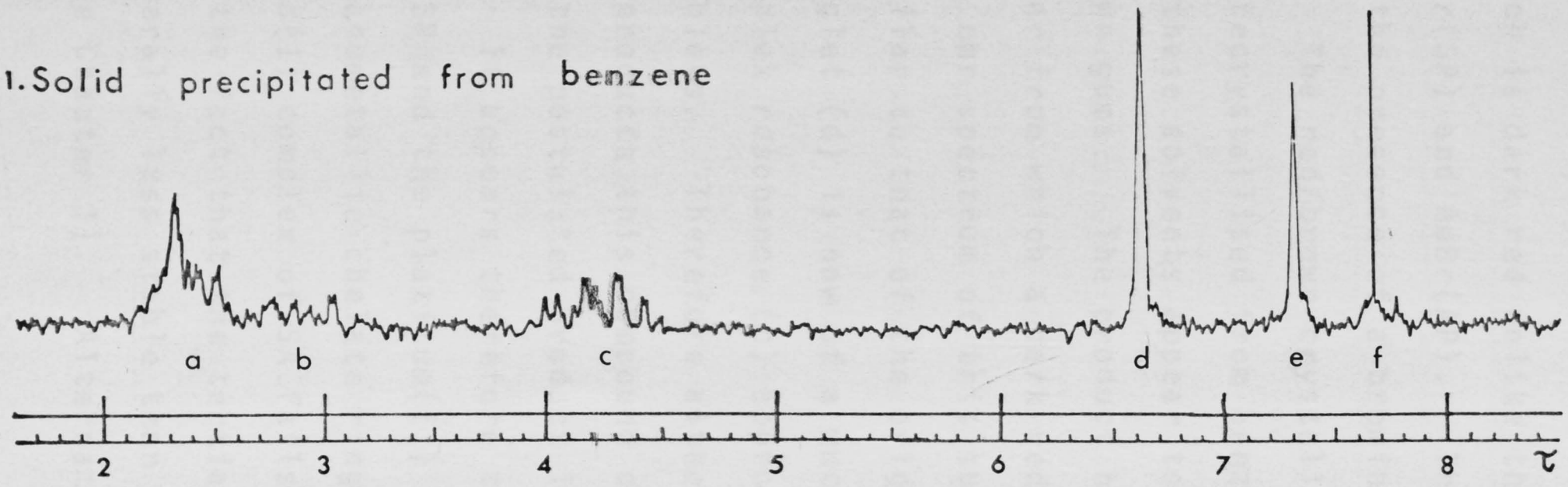
These spectra, together with the fact that the dark red colour is typical of gold(III) complexes containing $-AuBr_3$,[53] suggest that the main bromination product is the complex formed by oxidative-addition at the gold atom to give IX. This product is similar to one of the postulated bromination products of $PtBr_2(SA)_2$ written as VI.

IX

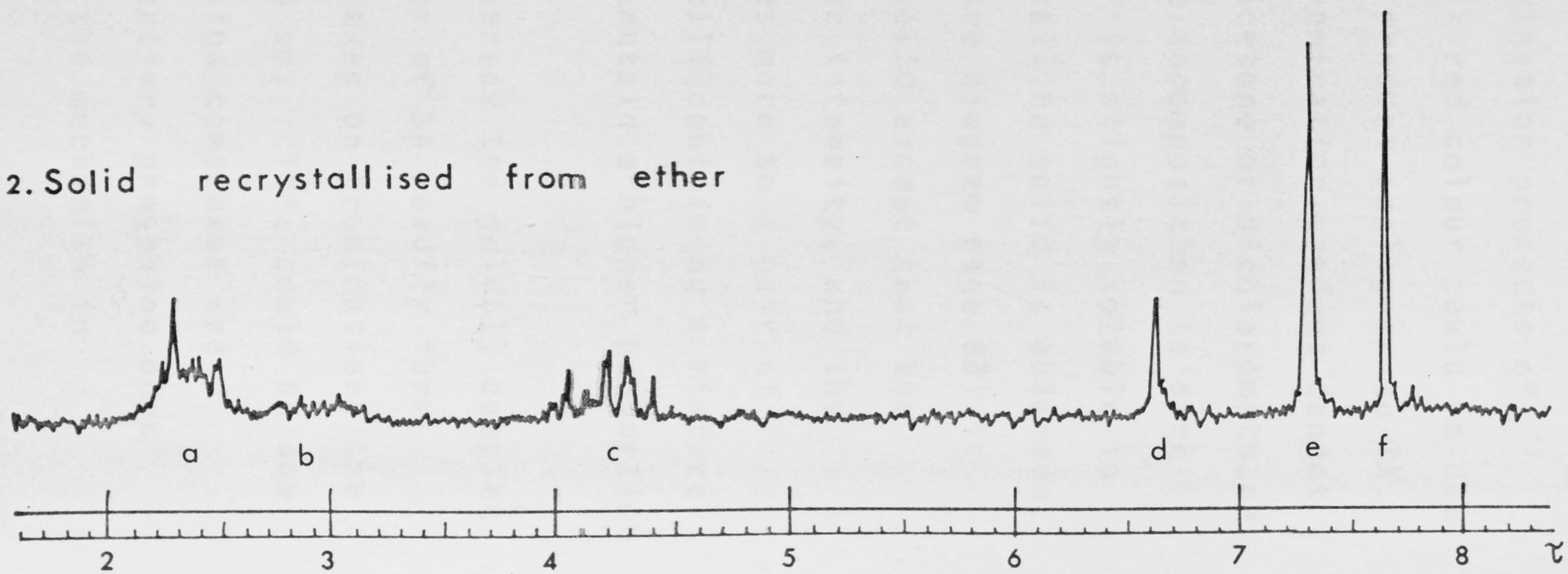


Nmr spectra of the bromination product of AuBr(SA)

1. Solid precipitated from benzene



2. Solid recrystallised from ether



The two methyl groups could be inequivalent thus accounting for two of the observed singlets, say (e) and (f), although it is difficult to account for the third singlet except by the presence of another bromination product. Kneen[32] found that bromination of AuBr(AA) gives a product $AuBr_3$(AA) which is dark red unlike the bromination products of AuBr(SP) and AuBr(AP). This dark red colour could be due to the presence of a bromination product analogous to IX.

The red/brown crystalline bromination product cannot be recrystallised from benzene, acetone or dichloromethane as these solvents appear to cause decomposition to dark brown gums. The product however is slightly soluble in ether from which a dark red crystalline solid is obtained. The nmr spectrum of this solid (see diagram page 63) is similar to that of the original solid except that the singlet (d) is now of a much lower intensity, and the complex resonance (c) approximates more to a pair of doublets. Therefore although still containing a mixture of products this compound could contain a higher proportion of the postulated product IX.

It appears therefore that whereas the gold(I) complex of SP and the platinum(II) complex of SA readily form organometallic chelate ring complexes on bromination, the gold(I) complex of SA fails to do so. This could be due to the fact that the tertiary arsine complexes are generally less stable than the tertiary phosphine ones (see Chapter I). Alternatively the mechanism in

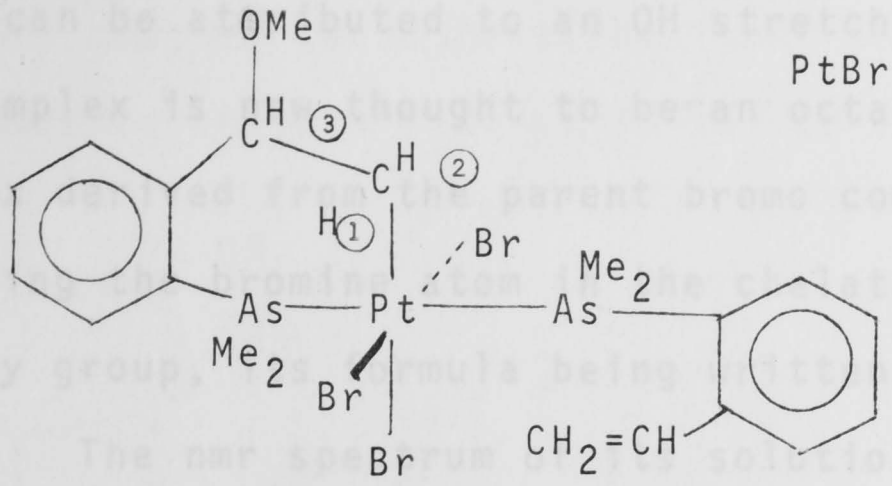
bromination is different for the gold(I) and platinum(II) atoms in the presence of arsenic and phosphorus donor ligands. The latter possibility will be discussed in Chapter IV.

E. Reactions of the organometallic platinum(IV) complex derived from *o*-styryldimethylarsine.

(i) $PtBr_3(SABr)(SA) + CH_3OH, C_2H_5OH$.

The compounds $PtBr_3(SAOEt)(SA)$ and $PtBr_3(SAOMe)(SA)$ (*6*c) are prepared by alcoholysis of the bromination product (*3*c) as described,[4] pure complexes being obtained in each case even though the bromination product apparently contains a mixture. The complex $PtBr_3(SAOEt)(SA)$ contains a six membered chelate ring, as shown by an X-ray structure determination,[3] and the ^{195}Pt decoupled 100 - MHz nmr spectrum of the chelate ring protons (see Table I) shows a typical ABX pattern (see page 48) as expected. On analysis (see Appendix) the difference between the chemical shifts of the $(-CH_2-)$ protons is found to be 29Hz compared with a coupling constant of 8.25Hz so that $\Delta\nu_{1,2}$ (29Hz) is less than $6J_{1,2}$ (6 x 8.25Hz).

The ^{195}Pt decoupled 100 - MHz nmr spectrum of the chelate ring protons in $PtBr_3(SAOMe)(SA)$ is also a typical ABX pattern (see Table I) so it is postulated that this complex also contains a six membered chelate ring as shown.



$PtBr_3(SAOMe)(SA)$

Analysis shows that $\Delta\nu_{1,2}$ is 20Hz which is still less than $6J_{1,2}$ (6 x 8.5Hz).

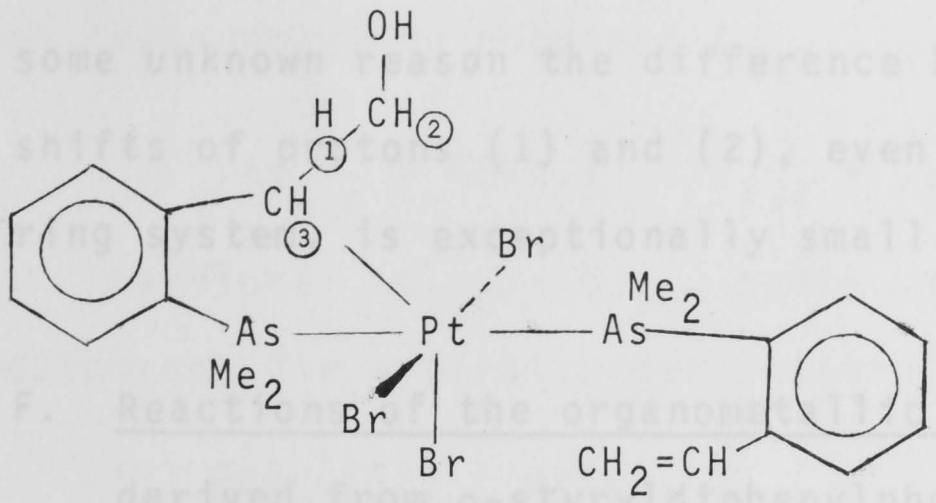
(ii) <u>$PtBr_3(SABr)(SA)$ + water</u>.

Various attempts were made to purify the complex $PtBr_3(SABr)(SA)$ since its nmr spectrum indicated that a mixture of products was present. Recrystallisation seemed ineffective, so chromatography was tried.

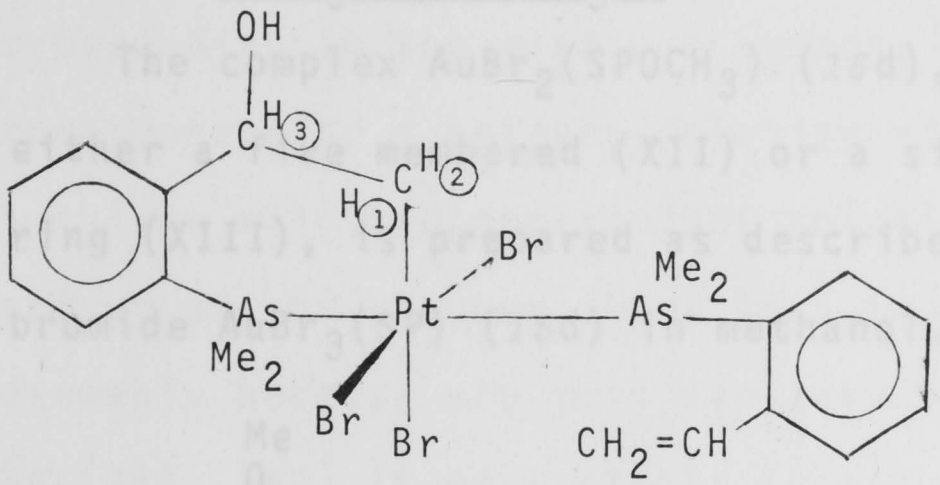
When a solution of the bromination product (*3*c) in benzene is chromatographed on a silica gel column with benzene/acetone solution, a pale yellow crystalline compound is obtained. At first this was thought to be the pure compound (*3*c) as its nmr spectrum (see Table I) shows the expected pair of doublets due to the uncoordinated β-vinyl protons. However this compound does not react with refluxing ethanol or methanol, and closer examination of its nmr spectrum reveals that the two resonances at *ca* 5.8τ and *ca* 6.7τ integrate in the ratio 1:3. These resonances were thought to be the chelate ring protons' resonances and would therefore be expected to integrate in the ratio 1:2. Since the IR spectrum of this complex shows a broad band in the region 3500 cm^{-1} - 3400 cm^{-1}

which can be attributed to an OH stretching frequency,[54] the complex is now thought to be an octahedral platinum(IV) complex derived from the parent bromo complex (*3*c) by replacing the bromine atom in the chelate ring by a hydroxy group, its formula being written as $PtBr_3(SAOH)(SA)$ (*19*c). The nmr spectrum of its solution containing D_2O shows $\tau(CDCl_3)$ 5.38(s,1,*H*OD), *ca* 5.8(m,1,>C*H*-), *ca* 6.7(m,2, -CH_2-) as well as resonances of the aromatic, β-vinyl and methyl protons. This shows that exchange between the hydroxy proton, the resonance of which previously lay under that of the chelate ring protons -CH_2- , and D_2O must have taken place, the resonances of the chelate ring protons now integrating correctly. In the IR spectrum there are bands at 1030 cm^{-1}, 1045 cm^{-1}, 1065 cm^{-1}, 1125 cm^{-1} and 1260 cm^{-1}, absent in the parent bromide, which could be due to OH deformation and CO stretching frequencies.[54] Analytical results (see Table X) indicate that the complex contains benzene of crystallisation which could not be removed even by pumping under vacuum. The same complex can also be prepared by refluxing the bromination product (*3*c) in aqueous acetone when a pale yellow solid is precipitated. An analysis on this solid (see Table X) shows that it is impure but all attempts to recrystallise it only cause decomposition. The chelate complex $PtBr_2(SA)$ (*8*c) is formed hence an accurate analysis of the complex $PtBr_3(SAOH)(SA)$ has never been obtained.

This complex could contain either a five membered or a six membered chelate ring as in (X) or (XI).



(X)



(XI)

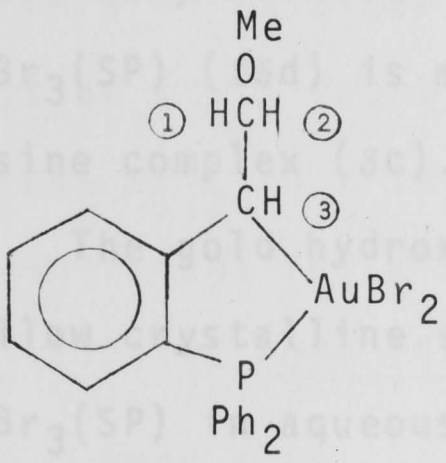
The ^{195}Pt decoupled 100 - MHz nmr spectrum of its solution containing D_2O shows a typical ABX pattern B (see Page 48); however the difference between the chemical shifts of the chelate ring protons (1) and (2), $\Delta\nu_{1,2}$, is very small (11Hz). Therefore in this case the nmr spectrum does not definitely differentiate between the possibility of a five or a six membered chelate ring, as this difference, $\Delta\nu_{1,2}$, is usually larger for a six membered chelate ring complex (see Table in Appendix). By comparison with the other products obtained by reacting the gold and platinum bromination products (*15*d) and (*3*c) with nucleophilic

reagents one would expect a six membered chelate ring complex to be formed. Therefore this complex probably has the six membered chelate ring structure XI but for some unknown reason the difference between the chemical shifts of protons (1) and (2), even though fixed in a ring system, is exceptionally small.

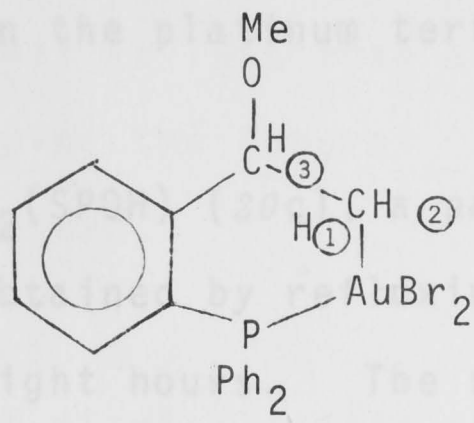
F. Reactions of the organometallic gold(III) complex derived from *o*-styryldiphenylphosphine.

(i) $AuBr_3(SP) + CH_3OH$.

The complex $AuBr_2(SPOCH_3)$ (*16*d), which could contain either a five membered (XII) or a six membered chelate ring (XIII), is prepared as described[32] by refluxing the bromide $AuBr_3(SP)$ (*15*d) in methanol.



(XII)



(XIII)

Kneen assigned the six membered chelate ring structure XIII on the basis of the nmr spectrum which shows three separate complex resonances of equal intensity for the chelate ring protons (see Table I). This indicates that protons (1) and (2) are in a fixed ring system and

therefore have very different chemical shifts. The ^{195}P decoupled 100 - MHz spectrum shows a typical AMX pattern C (see page 48), the difference between the chemical shifts of protons (1) and (2), $\Delta\nu_{1,2}$, being large compared with their coupling constant $J_{1,2}$.

i.e. $\Delta\nu_{1,2} = 68Hz.$; $J_{1,2} = 11Hz.$

Therefore $\Delta\nu_{1,2} > 6J_{1,2}$ hence satisfying the general requirement for a first order pattern.

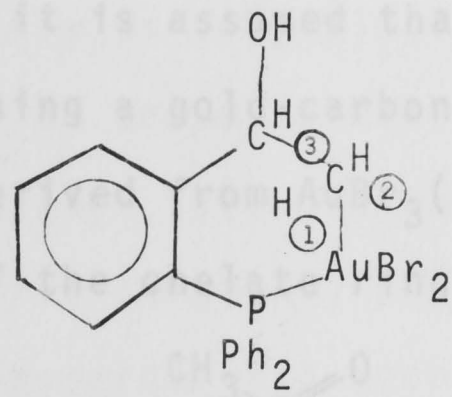
(ii) $\underline{AuBr_3(SP) + water}$.

An attempt was made to prepare the gold complex corresponding to the platinum hydroxy complex (*19*c) by chromatographing a benzene solution of $AuBr_3(SP)$ on a silica gel column with benzene/acetone solution. However the nmr spectrum of the product shows that it is unchanged $AuBr_3(SP)$, presumably because the gold tertiary phosphine complex $AuBr_3(SP)$ (*15*d) is more stable than the platinum tertiary arsine complex (*3*c).

The gold hydroxy complex $AuBr_2(SPOH)$ (*20*c), a pale yellow crystalline solid, can be obtained by refluxing $AuBr_3(SP)$ in aqueous acetone for eight hours. The nmr spectrum (see Table I) shows three separate complex resonances of equal intensity due to the chelate ring protons indicating a six membered chelate ring complex. The hydroxy proton gives a singlet at 8.3τ which shifts to 5.38τ on addition of D_2O showing that exchange has taken place. The IR spectrum has a broad band in the region 3500 cm^{-1} - 3000 cm^{-1} due to an OH stretching frequency

and also bands at 1280 cm^{-1}, 1050 cm^{-1}, 1075 cm^{-1} and 1100 cm^{-1} which could be OH deformation or CO stretching absorptions.[54] This complex is therefore probably the chelate ring complex (*20*c).

(*20*c)



The ^{195}P decoupled 100 - MHz nmr spectrum of the chelate ring protons appears to be the same as the AMX pattern C (see page 48) except that the two inner doublets of the quartets due to protons (1) and (2) are more intense than the outer ones. This indicates a deviation from a first order spectrum and on analysis as an ABX system it is found that $\Delta\nu_{1,2}$ (48Hz) is less than six times $J_{1,2}$ (6 x 12.5) thus satisfying the general requirement for a second order pattern.

(iii) $\underline{AuBr_3(SP) + CH_3COOH}$

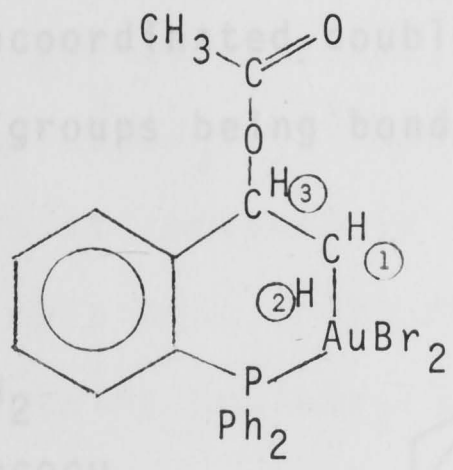
When $AuBr_3(SP)$ is refluxed in glacial acetic acid for eight hours a pale orange crystalline solid which analyses as $AuBr_2(SPOCOCH_3)$ is obtained.

Its IR spectrum shows a strong band at 1730 cm^{-1} due to a C=O stretching frequency and another strong band at 1240 cm^{-1} which is either a CO stretch or an OH deformation vibration.[55]

The nmr spectrum of the complex (see Table I) is very similar to that of $AuBr_2(SPOH)$ (*20*c) showing three separate complex resonances of equal intensity for the chelate ring protons, and a singlet at 8.66τ due to the methoxy protons.

Therefore it is assumed that this is a gold(III) complex containing a gold-carbon σ-bond in a six membered chelate ring derived from $AuBr_3(SP)$ by replacing the bromine atom of the chelate ring by an acetoxy group (*21*c).

(*21*c)

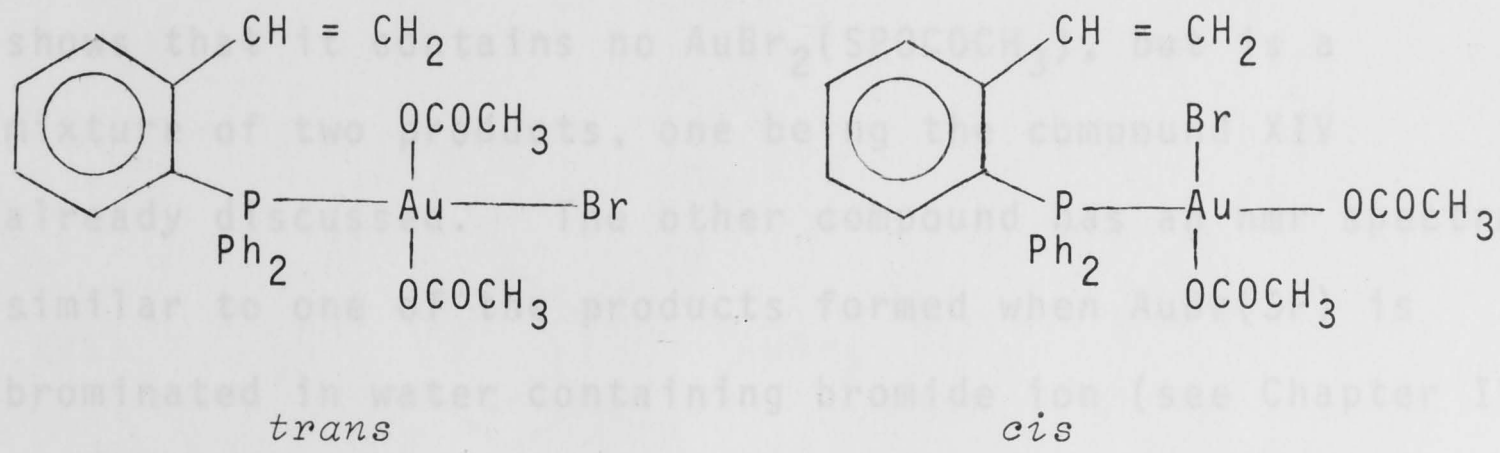


The ^{31}P decoupled nmr spectrum of the chelate ring protons is very similar to that obtained for $AuBr_2(SPOH)$, the same distortion occurring in the quartets due to the protons (1) and (2), indicating a second order system. Again on analysis it is found that $\Delta\nu_{1,2}$ (26Hz) is less than $6J_{1,2}$ (6 x 12.25Hz) satisfying the general requirement for a second order pattern.

If $AuBr_3(SP)$ is refluxed in glacial acetic acid for a longer period (three days), a second product is obtained in addition to $AuBr_2(SPOCOCH_3)$. The nmr spectrum of this product has a pair of doublets in the region 4.3τ - 5.0τ, due to uncoordinated β-vinyl protons similar to those seen in the nmr spectrum of AuBr(SP). However two of the peaks

are shifted upfield from 4.71τ and 4.76τ (as in AuBr(SP)) to 4.18τ and 4.92τ. There also appear to be complex resonances in the regions 1.8τ - 2.1τ and 2.9τ - 3.1τ which are partially obscured by the aromatic protons.

This spectrum is very similar to that of an intermediate postulated as being formed during the bromination of AuBr(SP) in methanol (see Chapter IV). This product could be a similar compound, *i.e.* a gold(III) complex containing an uncoordinated double bond in the styryl ligand, acetoxy groups being bonded directly to the gold atom (XIV).



trans *cis*

XIV

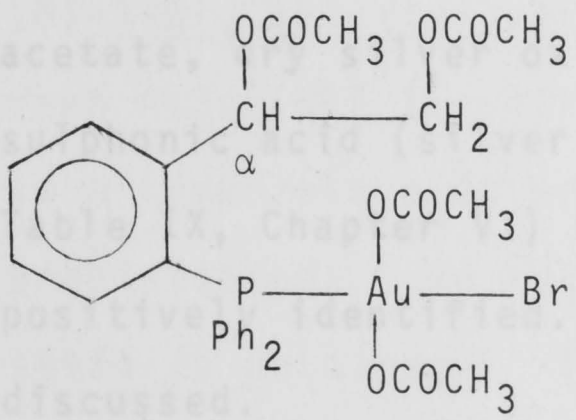
The nmr spectrum does show an additional singlet at 7.92τ which, if the pair of doublets is assumed to represent two protons, integrates approximately as six protons indicating that there are two acetoxy groups. Since only a singlet is observed either only one isomer is formed, or an equilibrium is maintained between the two structures in solution at room temperature.

The quality of the IR spectrum of the product is poor since it is a gum which will not mull easily. However it

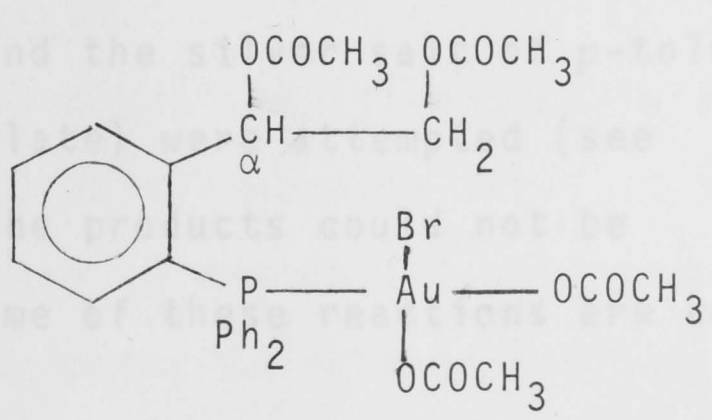
can be seen that the strong sharp band at 1730 cm^{-1} observed in the spectrum of $AuBr_2(SPOCOCH_3)$ has changed to a broad band in the region 1660 cm^{-1} - 1760 cm^{-1} indicating the presence of additional C=O stretching frequencies.

Although many metal acetoxy derivatives have been reported,[56] gold derivatives are rare. The monomeric gold(I) phosphine acetato complex $Ph_3PAu(OCOCH_3)$[57] has been prepared but the gold-oxygen bond is unstable and undergoes fission in the presence of acids. A dimeric gold(III) complex $[(CH_3)_2Au(OCOCH_3)]_2$[58] has also been reported.

If $AuBr_3(SP)$ is refluxed in acetic acid for ten days a yellow gum is obtained. The nmr spectrum of this gum shows that it contains no $AuBr_2(SPOCOCH_3)$, but is a mixture of two products, one being the compound XIV already discussed. The other compound has an nmr spectrum similar to one of the products formed when AuBr(SP) is brominated in water containing bromide ion (see Chapter IV), *i.e.* $\tau(CDCl_3)$ 3.3(t,1), 5.5(d,2), 7.99, 8.03, 8.12 (3 x s,12). If similar to the bromination product, one possible structure for this compound would be XV.



trans



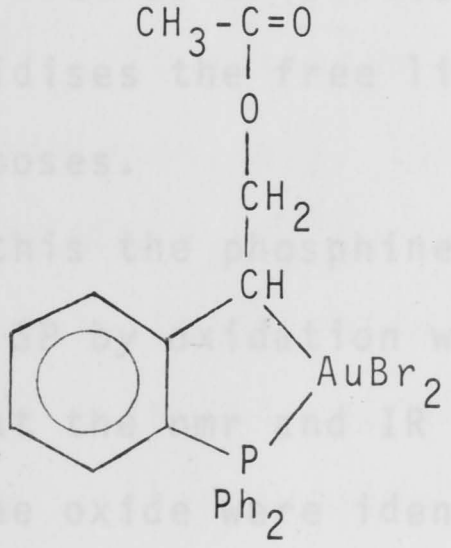
cis

XV

The substituted side chain protons would account for the doublet and triplet, while the three singlets integrating as twelve protons would account for the acetoxy protons. However, as explained previously, since the α-carbon atom is asymmetric the two protons on the β-carbon atom would be expected to give a more complex resonance than the doublet observed.

One other possibility is that the six membered chelate ring complex $AuBr_2(SPOCOCH_3)$ has isomerised to a five membered chelate ring complex XVI, although again one would expect a more complex resonance for the chelate ring protons.

XVI

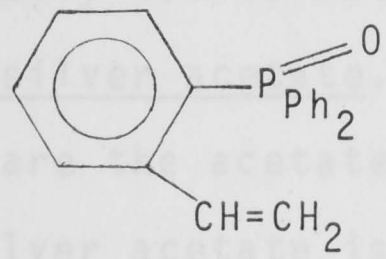


(iv) <u>$AuBr_3$(SP) and other nucleophilic reagents</u>.

The reactions of $AuBr_3(SP)$ with phenol, dry silver acetate, dry silver oxide and the silver salt of *p*-toluene sulphonic acid (silver tosylate) were attempted (see Table IX, Chapter VI) but the products could not be positively identified. Some of these reactions are now discussed.

(a) $\underline{AuBr_3(SP) + \text{dry } Ag_2O}$.

The nmr spectrum of the product (see Table IX) shows a pair of doublets similar to that observed in the spectrum of XIV and in the postulated bromination intermediate (see Chapter IV). However in this case the product is probably the phosphine oxide XVII and not a gold(III) complex.

XVII 

Silver oxide is used as an oxidising agent[59] and presumably in this case oxidises the free ligand which is formed as $AuBr_3(SP)$ decomposes.

To verify this the phosphine oxide XVII was prepared from the ligand SP by oxidation with hydrogen peroxide. It was found that the nmr and IR spectra of the product and the phosphine oxide were identical, both compounds showing a strong band in the IR at 1190 cm^{-1} assignable to a P=O stretching frequency.[60]

(b) $\underline{AuBr_3(SP) + \text{silver tosylate}}$.

When $AuBr_3(SP)$ is stirred with undried silver tosylate at room temperature in acetone, silver bromide is precipitated. On evaporation to dryness, a pale green-grey solid is obtained. The nmr spectrum of this solid shows that it is mainly the hydroxy compound $AuBr_2(SPOH)$ (*20*c) although there are additional resonances in the region

4.6τ - 6.5τ which cannot be identified, and a sharp singlet at 7.62τ probably due to methyl protons.

The nmr spectrum of the product obtained using silver tosylate which has been dried at $25^{o}/10$ mm^{-3} for 24 hours shows that a small amount of $AuBr_2(SPOH)$ is still present. This nmr spectrum also shows complex resonances in the region 4.6τ - 6.5τ and in addition two sharp singlets at 7.37τ and 7.62τ probably due to methyl protons.

(c) $AuBr_3(SP)$ + dry silver acetate.

It was hoped to prepare the acetate $AuBr_2(SPOCOCH_3)$ (*21*c) by this method as silver acetate is used as a standard reagent in organic synthesis to replace bromine atoms by acetoxy groups.[61] It has been used in this way to prepare metal acetoxy complexes, *e.g.* the dimeric dimethyl gold(III) acetate $[(CH_3)_2Au(OCOCH_3)]_2$[58] is prepared by the addition of silver acetate to the bromide $[(CH_3)_2AuBr]_2$.

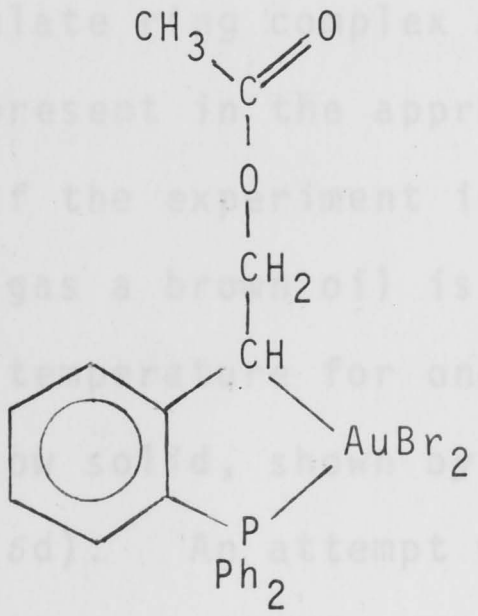
When $AuBr_3(SP)$ is stirred with dry silver acetate at room temperature, silver bromide is precipitated and the filtrate gives a grey/white solid on evaporation to dryness. The nmr spectrum of this solid shows that it contains some unchanged $AuBr_3(SP)$ together with another compound that gives a complex resonance at 6.0τ and sharp singlets at 7.88τ and 8.72τ. Its IR spectrum shows a strong broad band in the region 1580 cm^{-1} - 1630 cm^{-1} and another weaker band at 1730 cm^{-1} possibly due to either CO stretching or OH deformation vibrations.

When the reaction is repeated using excess dry silver acetate a solid is obtained that has an nmr spectrum showing singlets at 7.92τ, 8.26τ, 8.50τ, 8.64τ as well as 8.72τ, together with several complex resonances in the region 4.7τ - 7.5τ which are not clearly defined.

Possible products of these reactions, apart from the acetate (*21*c) are:-

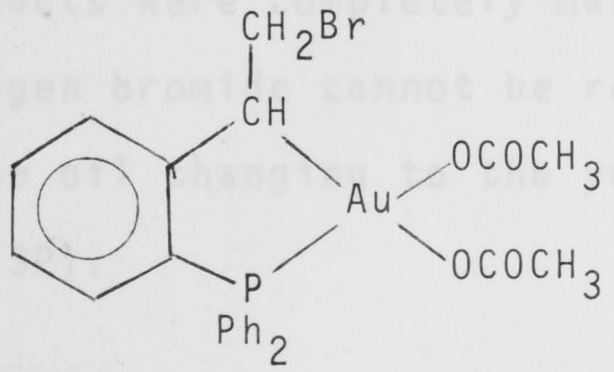
(XVIII) a complex formed by replacing the bromine atom in the chelate ring of $AuBr_3(SP)$ by an acetoxy group without rearrangement to give a five membered chelate ring complex.

XVIII



(XIX) a complex formed by replacing the bromine atoms attached to the metal in $AuBr_3(SP)$ by acetoxy groups.

XIX



However neither of these products could be established from the spectra obtained.

G. <u>The reaction of the organometallic gold(III) and platinum(IV) hydroxy complexes with hydrogen bromide</u>.

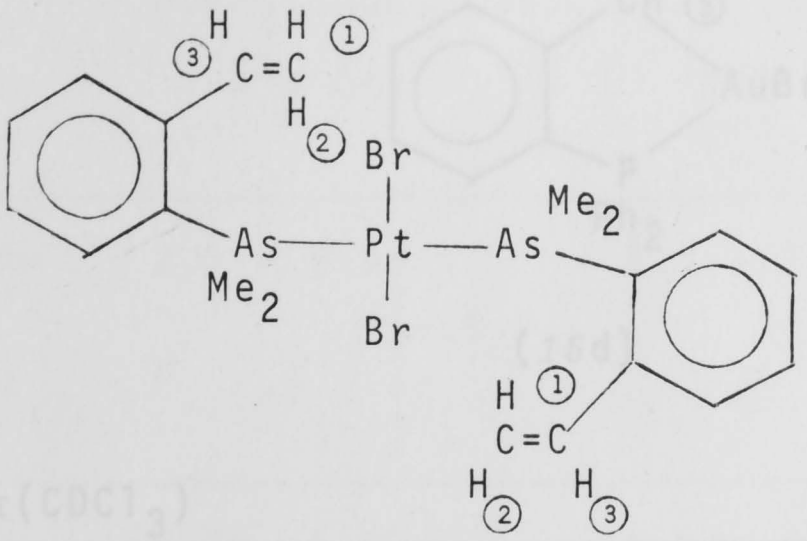
These reactions were an attempt to replace the hydroxyl groups in the hydroxy complexes by a bromine atom. Since these complexes probably contain six membered chelate rings it was hoped that the resulting bromides would also contain six membered chelate rings.

When the calculated amount of hydrogen bromide gas in carbon tetrachloride solution is added to $AuBr_2(SPOH)$ a pale yellow solid is obtained. The nmr spectrum of this solid shows that it contains unchanged $AuBr_2(SPOH)$ and the five membered chelate ring complex $AuBr_3(SP)$, the two compounds being present in the approximate ratio 20:1 respectively. If the experiment is repeated using excess hydrogen bromide gas a brown oil is obtained. If allowed to stand at room temperature for one week this slowly changes to a yellow solid, shown by its nmr spectrum to be pure $AuBr_3(SP)$ (*15*d). An attempt was made to obtain an nmr spectrum of the brown oil as this could possibly be an intermediate involved in the reaction, but it contained so much solvent and hydrogen bromide that any resonances due to other products were completely masked. The solvent and hydrogen bromide cannot be removed under vacuum without the oil changing to the yellow solid shown to be pure $AuBr_3(SP)$.

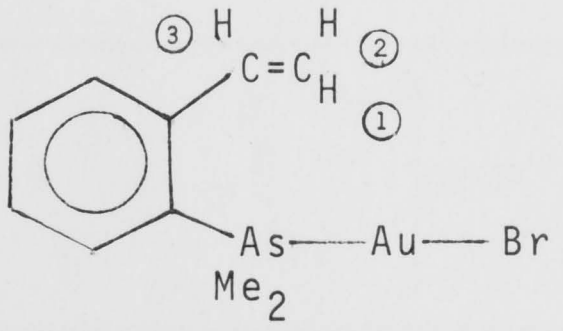
Similar reactions were attempted on the corresponding platinum complex $PtBr_3(SAOH)(SA)$ using both the calculated amount of hydrogen bromide and excess hydrogen bromide gas. Each experiment gives a yellow solid, the nmr spectra of which are very poorly defined. However these products do seem to be the original bromide $PtBr_3(SABr)(SA)$ (*3*c).

Therefore it appears that the bromides (*15*d) and (*3*c) can be obtained from the hydroxy complexes but only as the five membered chelate ring complexes. This rearrangement from a six membered chelate ring complex, as in the hydroxy derivatives, to a five membered chelate ring complex may involve a very unusual mechanism which is discussed in Chapter IV.

Nmr Table I



(2c)



(12c)

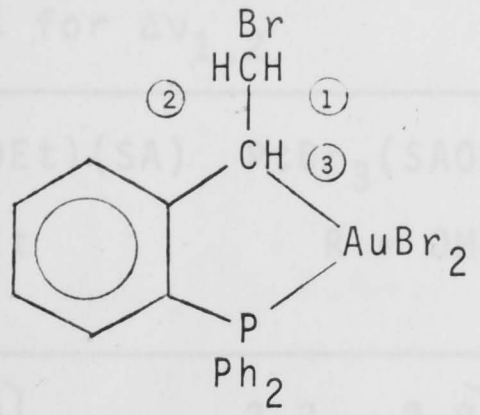
$\tau(CDCl_3)$

	Ar	$H_{③}$	$H_{①}$	$H_{②}$	Me
$PtBr_2(SA)_2$ (2c)	2.1 - 3.5 m,5	(i)	4.20, 4.37, 4.46, 4.57 dd,2		8.30 s,6 (ii)
AuBr(SA) (12c)	2.4 - 2.7 m,5	(i)	4.20, 4.36, 4.44, 4.55 dd,2		8.15 s,6

(i) lies under the aromatic resonance.

(ii) smaller singlet at 8.20τ appearing as shoulder on main resonance probably indicates the presence of isomers.

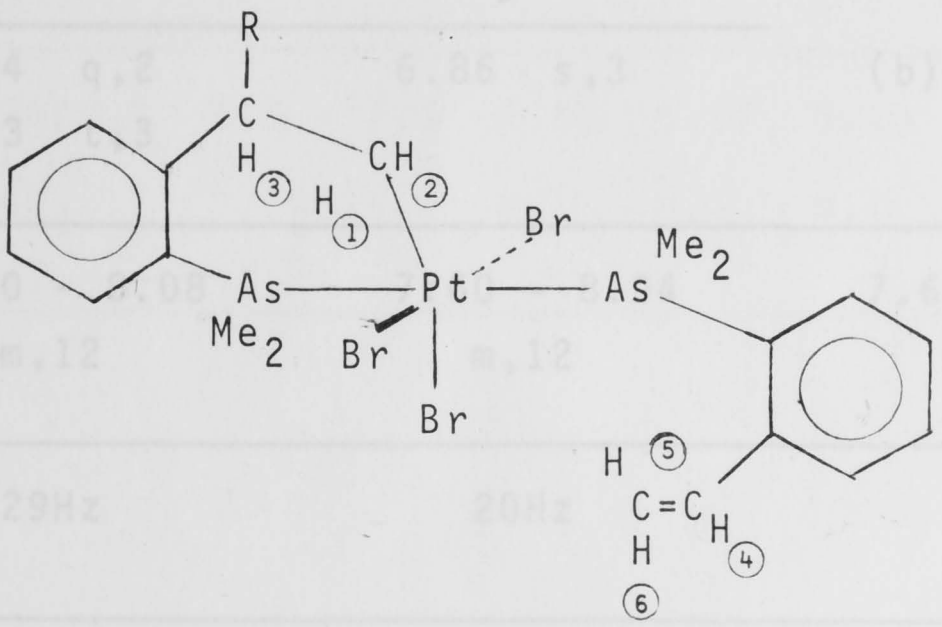
Nmr Table I



(*15*d)

$\tau(CDCl_3)$

	Ar	H ③	H ① H ②
$AuBr_3$(SP) (*15*d)	1.8 - 2.8 m,14	*ca* 4.5 m,1	*ca* 5.8 m,2



Nmr Table I

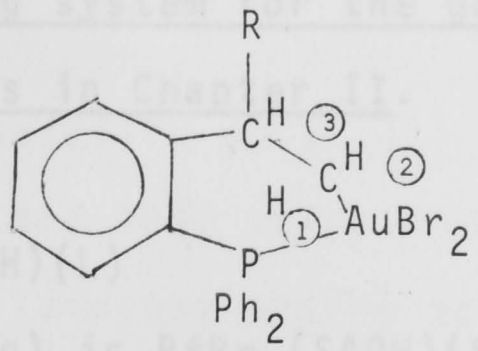
$\tau(CDCl_3)$ except for $\Delta\nu_{1,2}$

	$PtBr_3(SAOEt)(SA)$ R = OEt	$PtBr_3(SAOMe)(SA)$ R = OMe	$PtBr_3(SAOH)(SA)$ R = OH
Ar	2.3 - 2.9 m,9	2.3 - 2.9 m,9	2.2 - 3.0 m,9
H ④	(a)	(a)	(a)
H ⑤	4.22, 4.40 dd,2	4.22, 4.40 dd,2	4.20, 4.38 dd,2
H ⑥	4.54, 4.64	4.54, 4.64	4.52, 4.63
H ③	5.47 m,1	5.62 m,1	5.82 m,1
H ①	6.86 m,2	6.84 m,2	6.65 m,3
H ②	7.15	7.04	6.76
R	6.64 q,2 8.93 t,3	6.86 s,3	(b)
Me	7.60 - 8.08 m,12	7.60 - 8.04 m,12	7.60 - 7.90 m,12
$\Delta\nu_{1,2}$	29Hz	20Hz	11Hz

(a) lies under the aromatic protons.

(b) lies under the complex resonance due to $H_{①}$, $H_{②}$.

Nmr Table I



$\tau(CDCl_3)$ except for $\Delta\nu_{1,2}$

	Ar	H ③	H ①	H ②	R	$\Delta\nu_{1,2}$
$AuBr_2(SPOCH_3)$	1.8 - 2.7	4.61	6.39,	5.72	7.10	67Hz
R = OCH_3	m,14	m,1	m,1	m,1	s,3	
$AuBr_2(SPOH)$	1.8 - 2.8	4.60	5.59,	6.07	8.29	49Hz
R = OH	m,14	m,1	m,1	m,1	s,1	
$AuBr_2(SPOCOCH_3)$	1.8 - 2.8	4.60	5.17,	5.43	8.66	26Hz
R = $OCOCH_3$	m,14	m,1	m,1	m,1	s,3	

Numbering system for the gold and platinum complexes in Chapter II.

(*19*) $PtBr_3(LOH)(L)$

e.g. (*19*c) is $PtBr_3(SAOH)(SA)$,

$\overline{PtBr_3[o\text{-}LC_6H_4CHOHCH_2}][o\text{-}LC_6H_4CH{=}CH_2]$, L = $AsMe_2$

(*20*) $AuBr_2(LOH)$

e.g.(*20*d) is $AuBr_2(SPOH)$,

$\overline{AuBr_2[o\text{-}LC_6H_4CHOHCH_2}]$, L = PPh_2

(*21*) $AuBr_2(LOCOCH_3)$

e.g.(*21*d) is $AuBr_2(SPOCOCH_3)$,

$\overline{AuBr_2[o\text{-}LC_6H_4CHOCOCH_3CH_2}]$, L = PPh_2

CHAPTER III

Organometallic gold(III) and platinum(IV) chloro and iodo compounds derived from *o*-styryldimethylarsine and *o*-styryldiphenylphosphine

A. Preparation of the gold(III) and platinum(IV) complexes

B. Reactions of the organometallic gold(III) complex $AuCl_3(SP)$

C. The size of the chelate ring in $AuBr_3(SP)$, $AuCl_3(SP)$, $AuBr_2(SPOCH_3)$ and $AuCl_2(SPOCH_3)$

Nmr table II

Numbering system for the gold and platinum complexes in Chapter III.

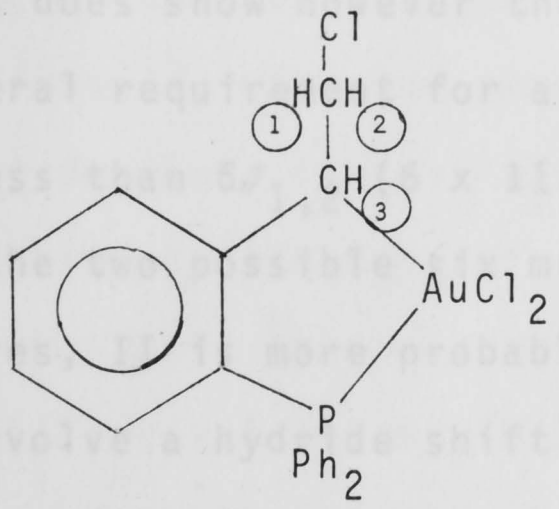
A. Preparation of the gold(III) and platinum(IV) chloro and iodo compounds derived from *o*-styryldimethylarsine and *o*-styryldiphenylphosphine.

1. Preparation of the organometallic gold(III) chloro complex $AuCl_3(SP)$.

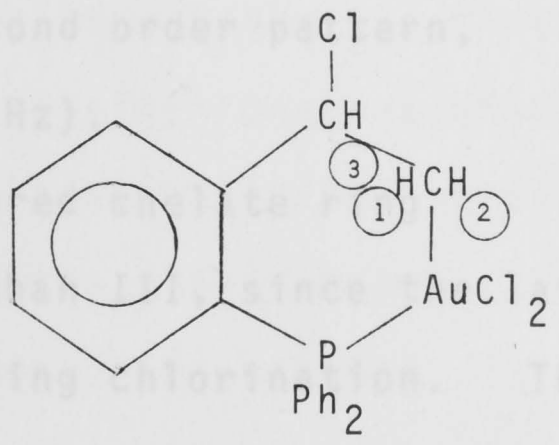
The complex AuCl(SP) is prepared by the addition of one mole of the ligand SP, to one mole of the complex ion $[AuCl_2]^-$, prepared by the reduction of sodium tetrachloroaurate(III) with sodium metabisulphite in the presence of excess lithium chloride.[32] It is a colourless crystalline compound, the nmr spectrum of which (see table II) shows a pair of doublets typical of the uncoordinated β-vinyl protons in the double bond of the ligand.

When this complex is treated with chlorine in benzene or carbon tetrachloride, a very pale yellow crystalline solid is obtained which analyses as $AuCl_3(SP)$. It is important that dry reagents are used in the preparation otherwise it is found that the yield is reduced as decomposition to gold occurs. The IR spectrum of this solid shows no bands at 930 cm^{-1} and 980 cm^{-1} due to $=CH_2$ and =CH- out-of-plane deformations.[36] Instead new bands appear at 720 cm^{-1} and 765 cm^{-1} which could be due to C-Cl stretching absorptions.[62] Therefore by comparison with the bromination product $AuBr_3(SP)$ (*15*d), this is probably a gold(III) organometallic complex

containing a gold-carbon σ-bond in a five or a six membered chelate ring. (22d)

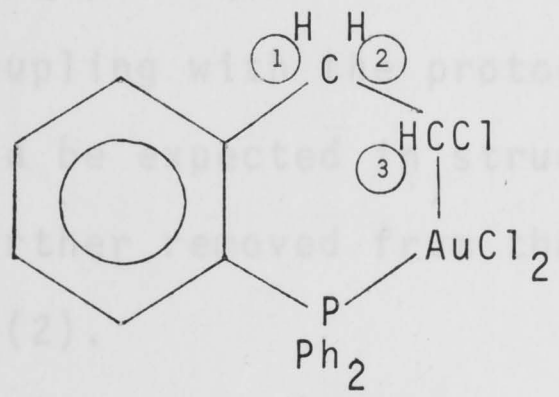


I



II

(22d)



III

The nmr spectrum of the compound (see table II) shows three separate complex resonances of equal intensity, each corresponding to one proton, for the chelate ring protons. This indicates one of the six membered chelate ring structures II or III.

The ^{31}P decoupled nmr spectrum of the chelate ring protons shows a typical ABX pattern B (see page 48) except that the complex resonance at 4.73τ due to the >CH- proton remains complex and does not collapse to a quartet on ^{31}P decoupling. This makes the spectrum

difficult to analyse (see Appendix) and must be due to additional coupling with the aromatic ring protons. Analysis does show however that $\Delta\nu_{1,2}$ (47 Hz) satisfies the general requirement for a second order pattern, being less than $6J_{1,2}$ (6 x 11.75 Hz).

Of the two possible six membered chelate ring structures, II is more probable than III, since the latter would involve a hydride shift during chlorination. This is confirmed by the change observed in the nmr spectrum as it is ^{31}P decoupled. Protons (1) and (2) have ^{31}P coupling constants of 1.5 Hz and 2.5 Hz while the corresponding coupling with the proton (3) is negligible. This effect would be expected in structure II where proton (3) is further removed from the ^{31}P nucleus than protons (1) and (2).

Therefore, unlike $AuBr_3(SP)$ (*15*d), shown to contain a five membered chelate ring, it appears that $AuCl_3(SP)$ has the six membered chelate ring structure shown in (*22*d II). This implies that chlorination and bromination of the gold(I) complexes AuX(SP) (X = Cl,Br) must proceed by different mechanisms, (see Chapter IV).

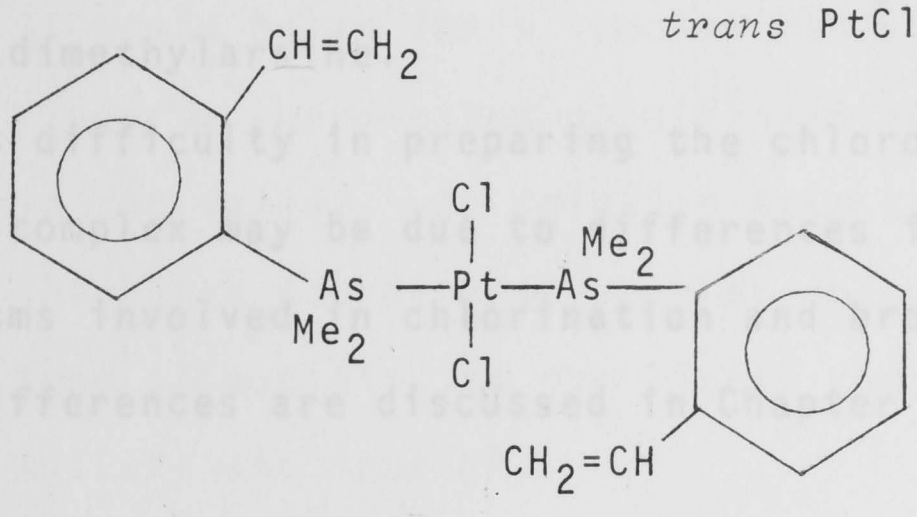
2. Attempted preparation of the organometallic platinum(IV) chloro complex

A pale yellow crystalline complex, of formula $PtCl_2(SA)_2$, is prepared by the addition of two moles of the ligand SA to one mole of platinous chloride in

chloroform. Its IR spectrum shows a band at 1630 cm^{-1} due to a C=C stretching vibration and bands at 920 cm^{-1} and 990 cm^{-1} due to $=CH_2$ and =CH- out-of-plane deformations.[36] The nmr spectrum (see table II) shows a pair of doublets typical of the β-vinyl protons of the uncoordinated double bond of the ligand. It is therefore assumed that this is analogous to the planar bromo platinum(II) complex $PtBr_2(SA)_2$ (*2*c), and has the structure shown in (*23*c).

trans $PtCl_2(SA)_2$.

(*23*c)



The compound is probably a mixture of the *cis* and *trans* isomers, as indicated by the presence of a small shoulder at 8.28τ on the main singlet at 8.35τ due to the methyl protons in the nmr spectrum, although the pale yellow colour indicates that the main component is the *trans* isomer.[63]

An attempt was made to prepare the platinum(IV) chelate ring complex $PtCl_3(SACl)$ (SA), analogous to the bromo complex $PtBr_3(SABr)(SA)$ (*3*c), by oxidising $PtCl_2(SA)_2$ with one mole of chlorine in benzene, but no reaction appeared to take place. The nmr spectrum of

the yellow solid obtained shows that it contains mainly unchanged $PtCl_2(SA)_2$. There are some resonances in addition to those of $PtCl_2(SA)_2$, *i.e.* under the pair of doublets due to the uncoordinated β-vinyl protons at *ca* 5.4τ and 6.3-6.8τ, but these are poorly defined and difficult to assign. Some oxidation to a platinum(IV) complex may have taken place as the nmr spectrum also shows a fairly intense complex resonance in the region 7.8-8.2τ, which is typical of the methyl groups in the bromo platinum(IV) complexes derived from *o*-styryldimethylarsine.

This difficulty in preparing the chloro platinum(IV) chelate complex may be due to differences in the mechanisms involved in chlorination and bromination. These differences are discussed in Chapter IV.

3. Attempted preparation of a gold(III) iodo complex.

An attempt was made to prepare the complex AuI(SP) by adding one mole of the ligand SP to one mole of the complex ion $[AuI_2]^-$, prepared by the reduction of sodium tetrachloroaurate (III) with sodium metabisulphite in the presence of excess lithium iodide. This preparation gives a pale yellow crystalline solid, the IR spectrum of which has bands at 935 cm^{-1} and 975 cm^{-1} due to $=CH_2$ and =CH- out-of-plane deformations.[36] The nmr spectrum has a pair of doublets (see table II) which is typical of the uncoordinated β-vinyl protons of the ligand,

except that in this compound these resonances are at a higher field than those observed in AuBr(SP) and AuCl(SP). Analysis shows the compound to be $AuI(SP)_2$, and it is presumably analogous to the compounds $AuBrL_2$ (*14*), where L = SP, AP and MP, prepared by Kneen.[32] A molecular weight determination shows that $AuI(SP)_2$ dissociates in chloroform solution, similar to the complexes (*14*) leading to two possible structures for the iodo complex. These were postulated by Kneen for the chloro and bromo complexes (*14*).

(1) It could be an ionic species containing the linearly coordinated gold(I) ion $[Au(SP)_2]^+$ in the solid. In solution this changes to the three coordinated complex $AuI(SP)_2$ which then dissociates to the linear complex AuI(SP) and free SP.

$$[Au(SP)_2]^+I^- \xrightarrow{\text{solution}} AuI(SP)_2 \rightleftharpoons AuI(SP) + SP$$

(2) It could be a three coordinate gold complex in the solid state which then dissociates in solution as above.

On addition of iodine to a solution of $AuI(SP)_2$, a yellow solid is obtained. This has an nmr spectrum similar to that of the compound AuBr(SP) (see table II), *i.e.*, $\tau(CDCl_3)$ 4.34, 4.50, 4.66, 4.76 (dd,2 = CH_2) 2.3-3.3 (m,15, Ar + =C*H*-). The solid must therefore be the linear gold(I) complex AuI(SP) which is present in

solutions of $AuI(SP)_2$. Clearly iodine only reacts with the free ligand present in these solutions to form the halogenated ligand $o\text{-}CH_2{=}CHC_6H_4PPh_2I_2$, which probably then immediately hydrolyses to the phosphine oxide making its isolation difficult.

$$AuI(SP)_2 \rightleftharpoons AuI(SP) + SP \xrightarrow{I_2} SPI_2$$

Similar behaviour on the bromination of $AuBr(SP)_2$ was observed by Kneen.[32]

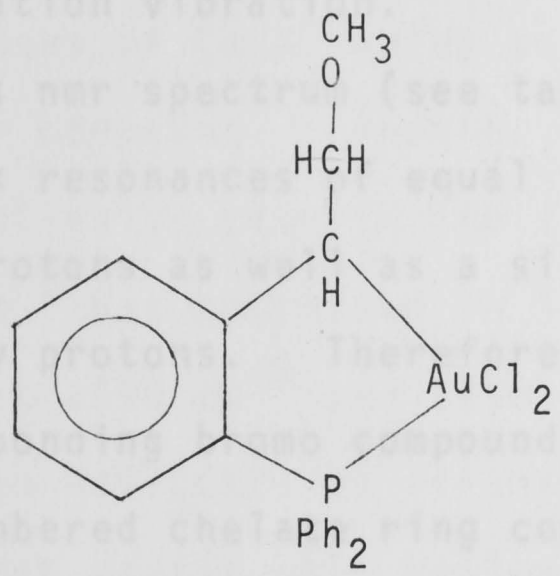
B. Reactions of the organometallic gold(III) complex $AuCl_3(SP)$

1. $AuCl_3(SP) + CH_3OH$.

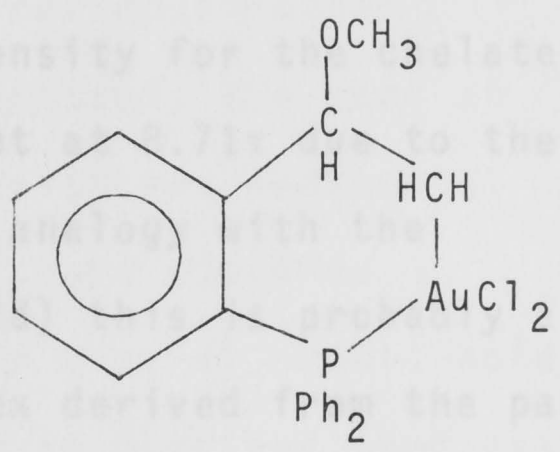
The complex $AuCl_3(SP)$ reacts very slowly with refluxing methanol, the reaction taking one week for completion. One reason for the slow reaction could be that alcoholysis of the five membered chelate ring complex $AuBr_3(SP)$ involves the primary group $-CH_2Br$, while alcoholysis of $AuCl_3(SP)$, thought to contain a six membered chelate ring, would involve the alcoholysis of a secondary group >CHCl. Alcoholysis of secondary halides is generally a slower reaction than alcoholysis of primary halides.[64]

Methanolysis of $AuCl_3(SP)$ gives white feathery crystals of formula $AuCl_2(SPOCH_3)$, which have a strong band at 1110 cm^{-1} due to a COC stretching vibration in their IR spectrum.[65] Therefore by analogy with the corresponding bromo compounds (*16*) this is probably a five or a six membered chelate ring complex derived from the parent chloro complex (*22*d) by replacing the chlorine atom of the chelate ring by the nucleophile OCH_3^- (*24*d).

(*24*d)



IV



V

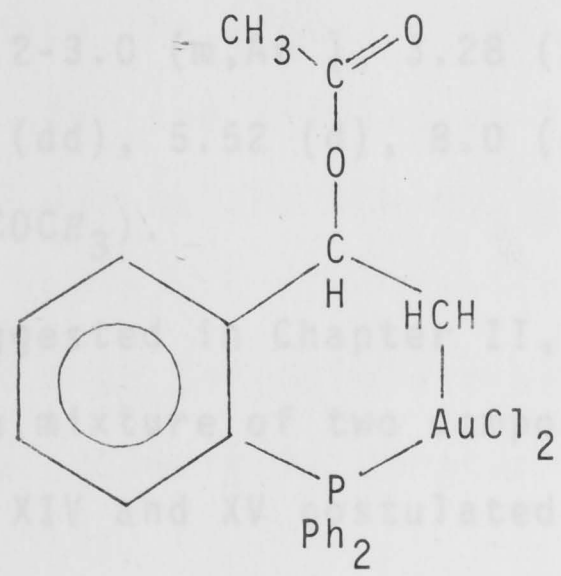
The nmr spectrum (see table II) shows three separate complex resonances of equal intensity for the chelate ring protons, indicating the six membered chelate ring complex V. The ^{31}P decoupled nmr spectrum of the chelate ring protons shows a typical AMX pattern C (see page 48) and inspection of the resonances shows that $\Delta\nu_{1,2}$ (70 Hz) is greater than $6J_{1,2}$ (6 x 11 Hz) thus satisfying the general requirements for a first order pattern.

2. $AuCl_3(SP)$ + CH_3COOH.

The reaction of $AuCl_3(SP)$ with refluxing glacial acetic acid is faster than that with refluxing methanol, a pale yellow crystalline solid analysing as $AuCl_2(SPOCOCH_3)$ being obtained after eight hours. The IR spectrum of this solid has a strong band at 1730 cm^{-1} due to a C=O stretching frequency and another strong band at 1220 cm^{-1} which is either a CO stretch or an OH deformation vibration.[55]

Its nmr spectrum (see table II) shows three separate complex resonances of equal intensity for the chelate ring protons as well as a singlet at 8.71τ due to the acetoxy protons. Therefore by analogy with the corresponding bromo compound (*21*d) this is probably a six membered chelate ring complex derived from the parent compound $AuCl_3(SP)$ by replacing the chlorine atom of the chelate ring by an acetoxy group (*25*d)

(*25*d)



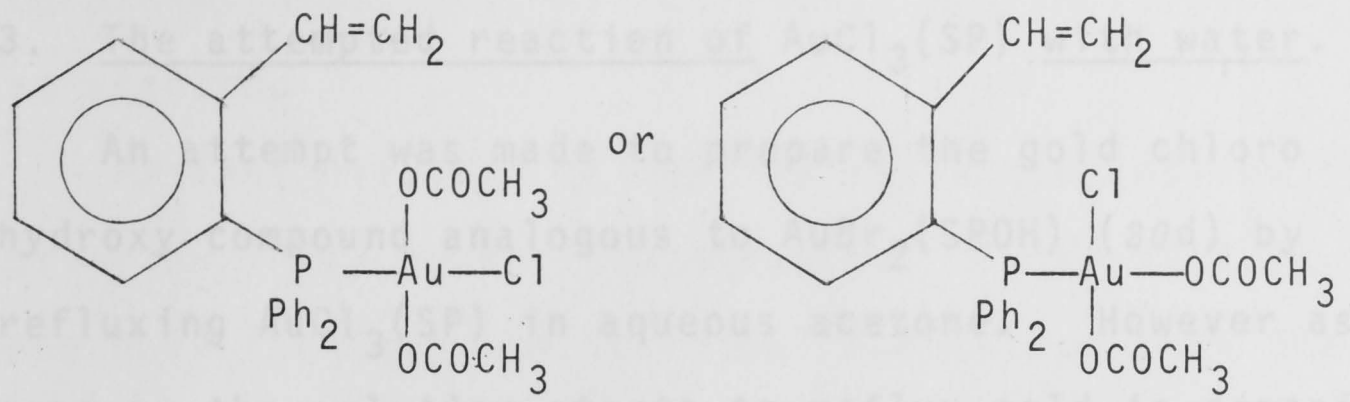
If the complex $AuCl_3(SP)$ is refluxed in glacial acetic acid for a longer period of time, the reaction

seems to follow the pattern observed for the reaction of $AuBr_3(SP)$ with glacial acetic acid (see Chapter II), except that this reaction appears to be faster than that with the bromide. After refluxing for three days the nmr spectrum of the solid is the same as that of $AuCl_2(SPOCOCH_3)$ with some additional singlets in the region 7.9-8.1τ indicating the presence of other acetoxy derivatives. There is also a series of poorly defined complex resonances lying under the chelate ring proton resonances of (*25*d) which suggest the presence of another compound. Another indication of other derivatives is seen in the IR spectrum; the band at 1730 cm^{-1} has increased in intensity and additional bands at 1190 cm^{-1} and 1250 cm^{-1} have appeared.

When $AuCl_3(SP)$ is refluxed in glacial acetic acid for seven days a pale yellow gum is obtained that has an nmr spectrum very similar to that obtained from the gum made by refluxing $AuBr_3(SP)$ in acetic acid for ten days.

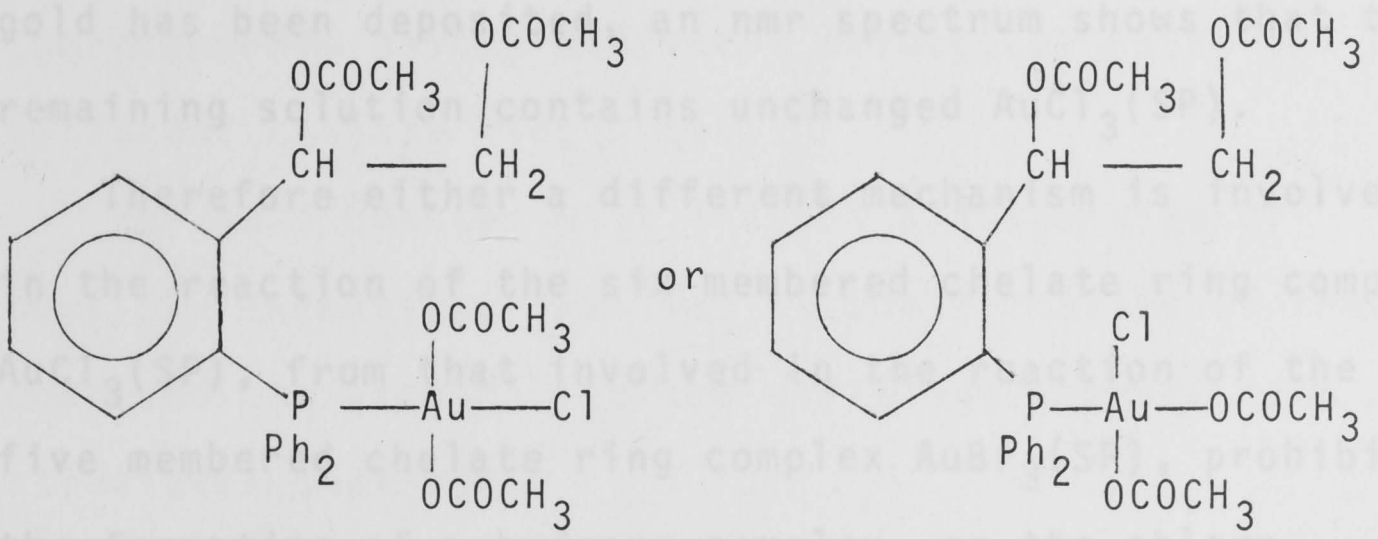
i.e., τ(CDCl) 2.2-3.0 (m,Ar), 3.28 (t), 4.35, 4.52, 4.82, 4.96 (dd), 5.52 (d), 8.0 (s, $OCOCH_3$), 8.04 (s, $OCOCH_3$).

Therefore, as suggested in Chapter II, the nmr spectrum could represent a mixture of two compounds, analogous to the compounds XIV and XV postulated as being formed after the prolonged reaction of $AuBr_3(SP)$ with glacial acetic acid. These compounds could be VI and VII.



VI

trans *cis*



VII

trans *cis*

The uncoordinated β-vinyl proton of VI would give the pair of doublets at 4.35-4.96τ, the α-vinyl proton probably being under the aromatic resonance. Compound VII would account for the triplet at 3.28τ and the doublet at 5.52τ, due to the >CH-CH_2- protons in the substituted side chain.

An attempt is made to postulate mechanisms to account for these products in Chapter IV.

3. The attempted reaction of $AuCl_3(SP)$ with water.

An attempt was made to prepare the gold chloro hydroxy compound analogous to $AuBr_2(SPOH)$ (*20*d) by refluxing $AuCl_3(SP)$ in aqueous acetone. However as soon as the solution starts to reflux gold is deposited on the sides of the flask, and if the reaction is stopped after three hours, when a considerable amount of gold has been deposited, an nmr spectrum shows that the remaining solution contains unchanged $AuCl_3(SP)$.

Therefore either a different mechanism is involved in the reaction of the six membered chelate ring complex $AuCl_3(SP)$, from that involved in the reaction of the five membered chelate ring complex $AuBr_3(SP)$, prohibiting the formation of a hydroxy complex, or the chloro hydroxy complex is formed initially but then immediately decomposes.

C. The size of the chelate ring in $AuBr_3(SP)$, $AuCl_3(SP)$, $AuBr_2(SPOCH_3)$ and $AuCl_2(SPOCH_3)$.

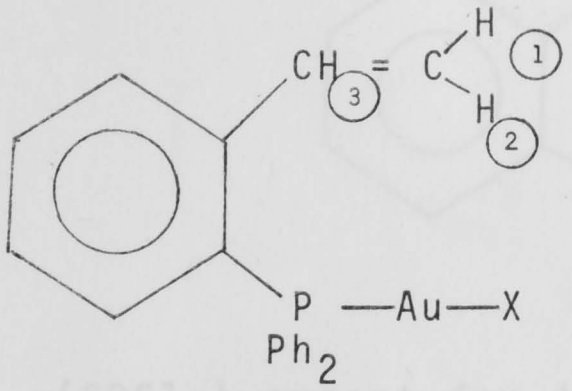
All nmr spectroscopic evidence indicates that $AuCl_3(SP)$, $AuBr_2(SPOCH_3)$ and $AuCl_2(SPOCH_3)$ contain a six membered chelate ring. In contrast an X-ray structure determination[39] has shown that $AuBr_3(SP)$ has a five membered chelate ring, and the nmr spectrum of the chelate ring protons in the latter complex is very different from that of the analogous spectrum in the

complexes $AuCl_3(SP)$, $AuBr_2(SPOCH_3)$ and $AuCl_2(SPOCH_3)$ as expected.

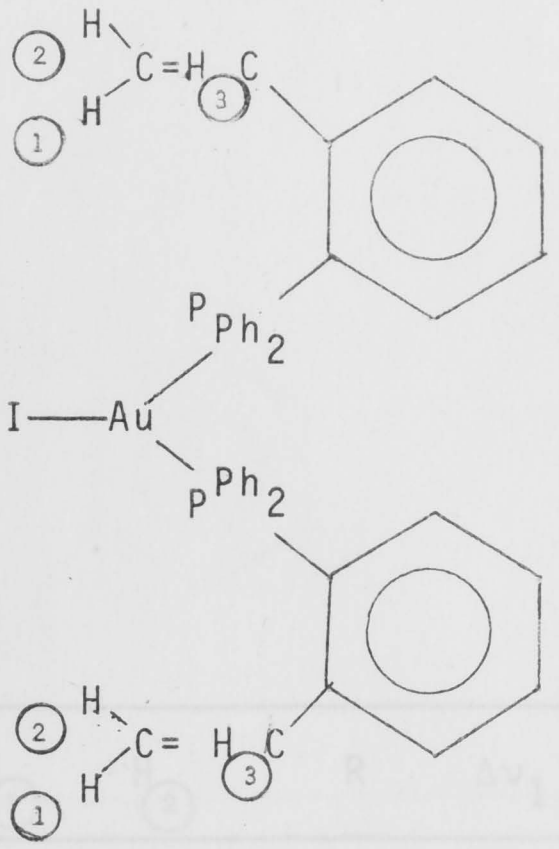
Further evidence to confirm these conclusions is given by X-ray powder photographs. Those of $AuCl_2(SPOCH_3)$ and $AuBr_2(SPOCH_3)$ are identical indicating that the compounds are isomorphous and probably isostructural. However the corresponding X-ray photographs of $AuBr_3(SP)$ and $AuCl_3(SP)$ are not identical, as would be expected for two compounds having different structures based on different chelate ring sizes.

The next Chapter will include a discussion of possible mechanisms involved in the formation of these compounds to account for the different chelate ring structures observed.

Nmr Table II



AuX(SP)



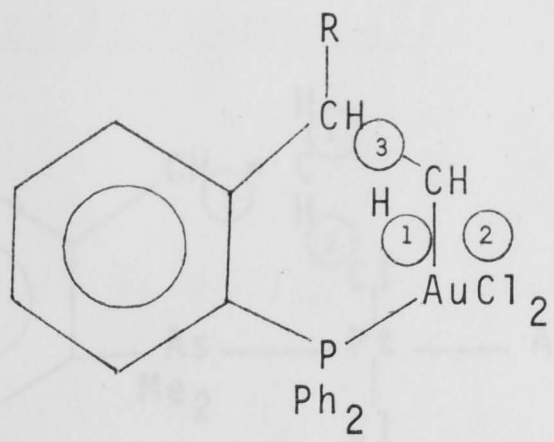
AuI(SP)$_2$

$\tau(CDCl_3)$

	Ar	H_3	H_1	H_2
AuCl(SP) X = Cl	2.0 - 3.0 (a) m,15		4.34, 4.50, 4.66, 4.77 dd,2	
AuBr(SP) X = Br	2.3 - 3.4 (a) m,15		4.37, 4.54. 4.71, 4.82 dd,2	
$AuI(SP)_2$	2.3 - 3.4 (a) m,30		4.52, 4.70, 4.94, 5.04 dd,4	

(a) under the aromatic protons.

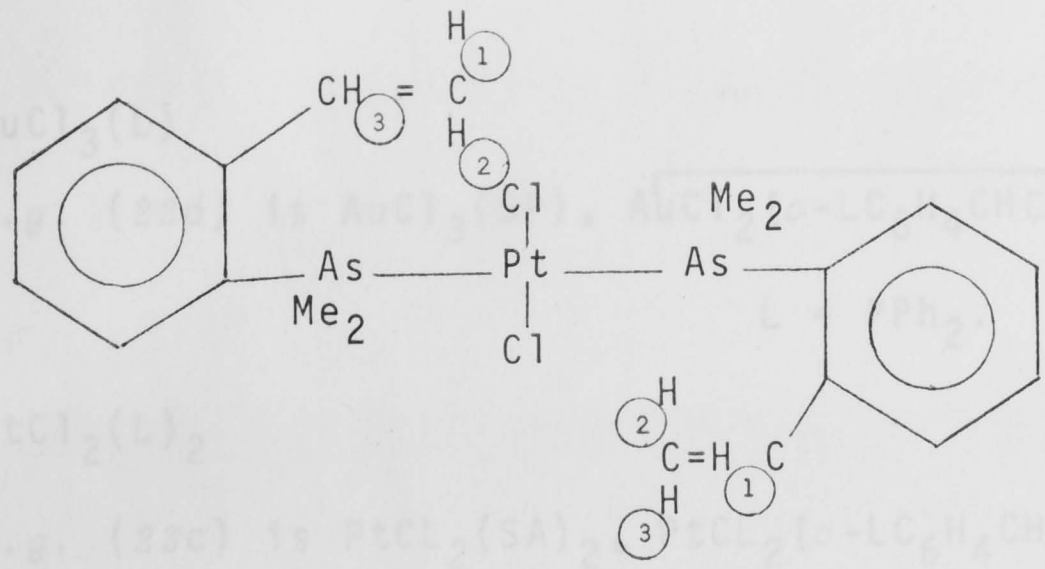
Nmr Table II



$\tau(CDCl_3)$ except for $\Delta\nu_{1,2}$

	Ar	$H_{(3)}$	$H_{(1)}$	$H_{(2)}$	R	$\Delta\nu_{1,2}$
$AuCl_3(SP)$	1.8-2.8	4.73	5.50	5.97	-	47 Hz
R = Cl	m,14	m,1	m,1	m,1		
$AuCl_2(SPOCH_3)$	1.8-2.8	4.87	5.80	6.50	7.10	70 Hz
$R = OCH_3$	m,14	m,1	m,1	m,1	s,3	
$AuCl_2(SPOCOCH_3)$	1.7-2.8	4.60	5.15	5.46	8.66	31 Hz
$R = OCOCH_3$	m,14	m,1	m,1	m,1	s,3	

Nmr Table II



	Ar	H_3	H_1	H_2	Me
$PtCl_2(SA)_2$	2.1-3.6 (a)		4.16, 4.34, 4.44, 4.45		8.35(b)
	m,10		dd,4		s,12

(a) under aromatic protons.

(b) shoulder at 8.28τ due to the presence of another isomer.

Numbering system for the gold and platinum complexes in Chapter III

(*22*) $AuCl_3(L)$

e.g. (*22*d) is $AuCl_3(SP)$, $\overline{AuCl_2[o\text{-}LC_6H_4CHClCH_2]}$

$L = PPh_2$.

(*23*) $PtCl_2(L)_2$

e.g. (*23*c) is $PtCL_2(SA)_2$, $PtCL_2[o\text{-}LC_6H_4CH{=}CH_2]_2$,

$L = AsMe_2$.

(*24*) $AuCl_2(LOCH_3)$

e.g. (*24*d) is $AuCl_2(SPOCH_3)$, $\overline{AuCl_2[o\text{-}LC_6H_4CHOCH_3CH_2]}$,

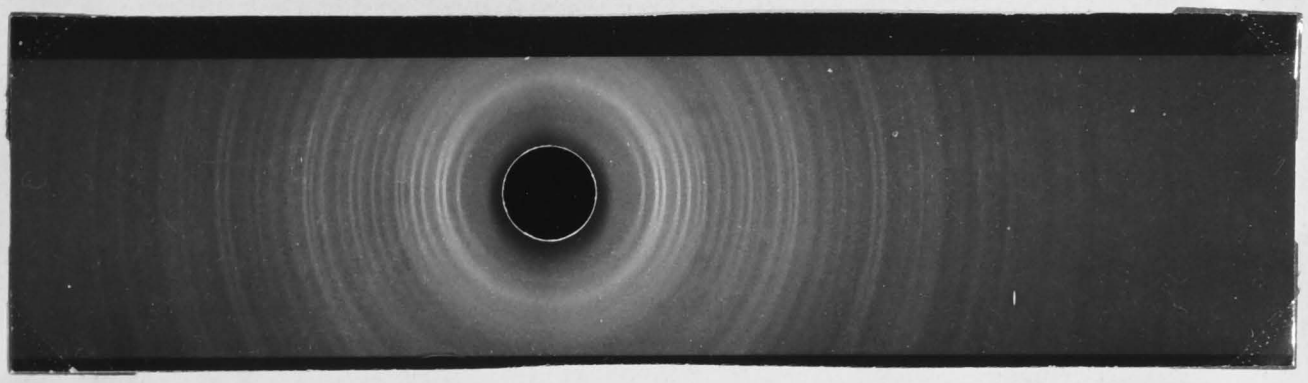
$L = PPh_2$.

(*25*) $AuCl_2(LOCOCH_3)$

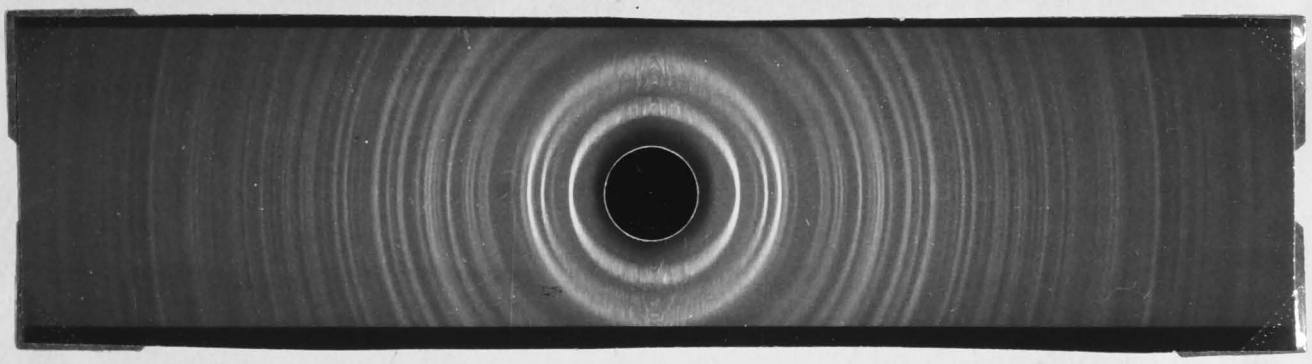
e.g. (*25*d) is $AuCl_2(SPOCOCH_3)$,

$\overline{AuCl_2[o\text{-}LC_6H_4CHOCOCH_3CH_2]}$, $L = PPh_2$.

X-ray powder photographs

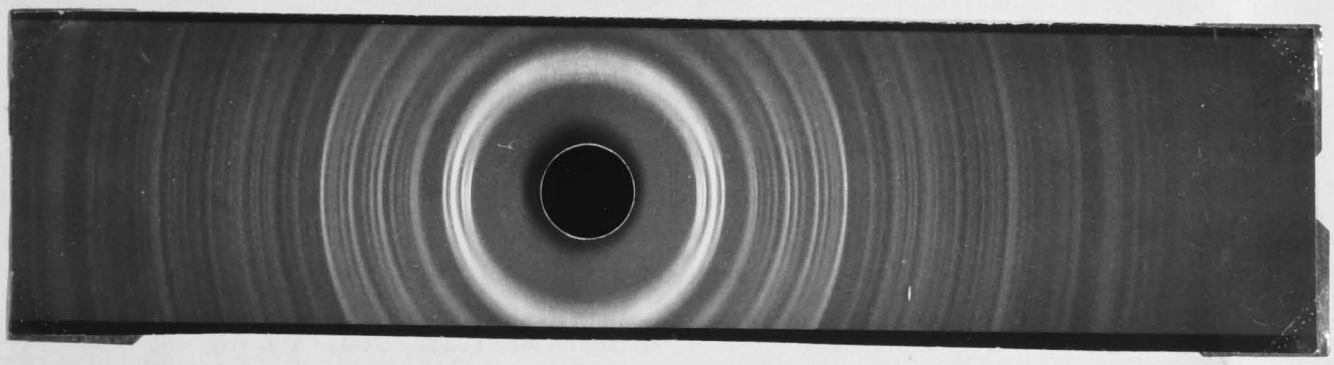


$AuCl_3(SP)$

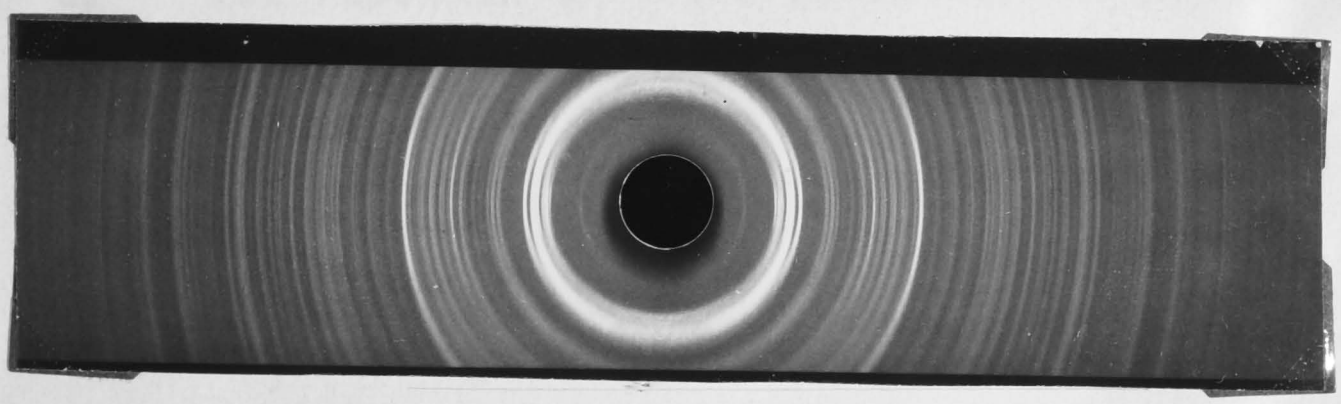


$AuBr_3(SP)$

X-ray powder photographs



$AuCl_2(SPOCH_3)$



$AuBr_2(SPOCH_3)$

CHAPTER IV

Possible mechanisms for the formation and reaction of gold(III) and platinum(IV) organometallic complexes derived from the ligands *o*-styryldimethylarsine and *o*-styryldiphenylphosphine.

A. Preparation of the organometallic complexes

(i) Bromination

(ii) Chlorination

B. Reactions of the organometallic complexes

C. The reaction of the organometallic gold(III) hydroxy complex with hydrogen bromide

Possible mechanisms for the formation and reaction of gold(III) and platinum(IV) organometallic complexes derived from the ligands *o*-styryldimethylarsine and *o*-styryldiphenylphosphine.

In this Chapter an attempt is made to postulate the various mechanisms involved in the preparation and reaction of the organometallic complexes described so far. To do this, comparisons are made with organic reactions involving halogenation and nucleophilic substitution. It must be appreciated however that the reactions of the organometallic complexes may not be strictly comparable mechanistically with these organic reactions and therefore any postulated mechanisms are purely speculative.

A. Preparation of the organometallic complexes

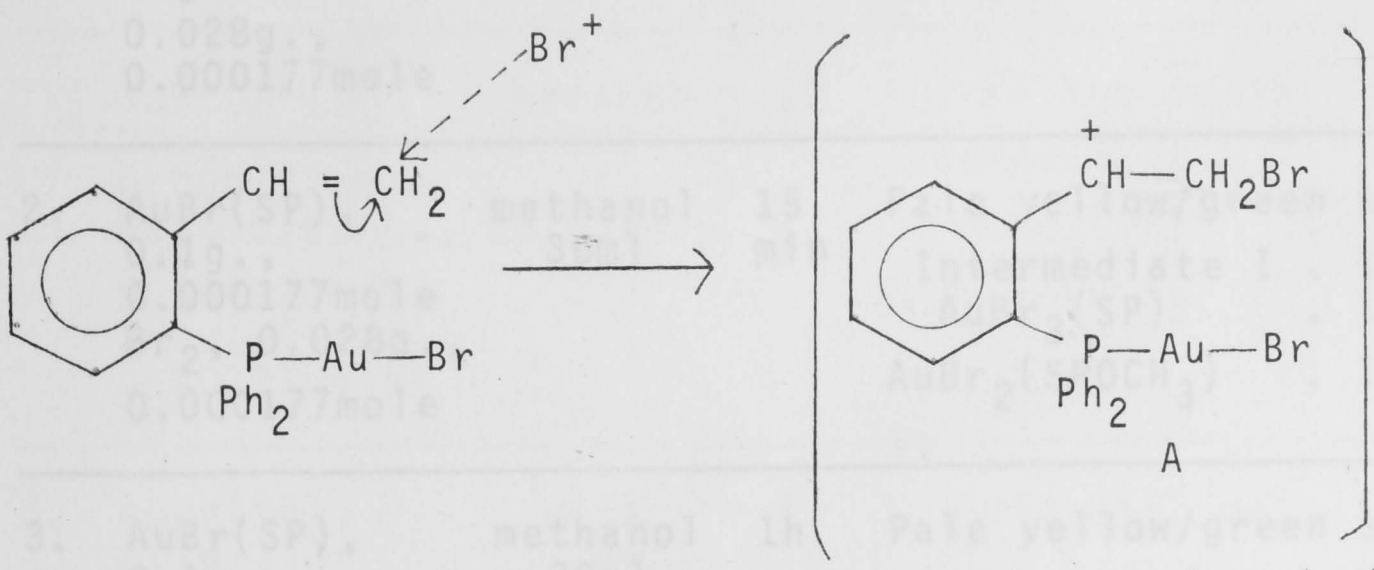
The work presented so far has shown that bromination of the gold(I) complex AuBr(SP) and the platinum(II) complex $PtBr_2(SA)_2$ leads to the formation of five membered chelate ring complexes, a metal-carbon σ-bond having been formed with the α-carbon atom in the side chain of the ligand. Chlorination of the gold(I) complex AuCl(SP) however gives a six membered chelate ring complex, a gold-carbon σ-bond having been formed with the β-carbon atom in the side chain of the ligand. An attempt will now be made to distinguish between the different mechanisms which give rise to these halogenation products.

(i) Bromination

The bromination of the gold(I) and platinum(II) complexes can be compared with either bromination of olefins[66] or the oxidative-addition of halogens to metal complexes.[16] Each of these alternatives will now be considered.

(1) Bromination of olefins

The usual mechanism postulated for bromination of olefins involves initial attack by the electrophile Br^+ to give a bromonium ion, then addition of the nucleophile Br^- to give the bromination product.[66] In the gold(I) complex AuBr(SP) attack could take place at the free olefinic double bond in the ligand to give the bromonium ion A.



To explain the formation of the five membered chelate ring complex $AuBr_3(SP)$ attack by Br^- must then take place at the gold atom.

TABLE III

Summary of bromination reactions

(1) In all reactions the product was obtained by either evaporating the solution to dryness or extracting the reaction mixture with chloroform and evaporating the dried extracts to dryness.

(2) The products were identified by their nmr spectra, the ratio of the products in reactions 2-3 and 5-7 being calculated approximately by assuming that the pair of doublets in the nmr spectrum of I represents two protons.

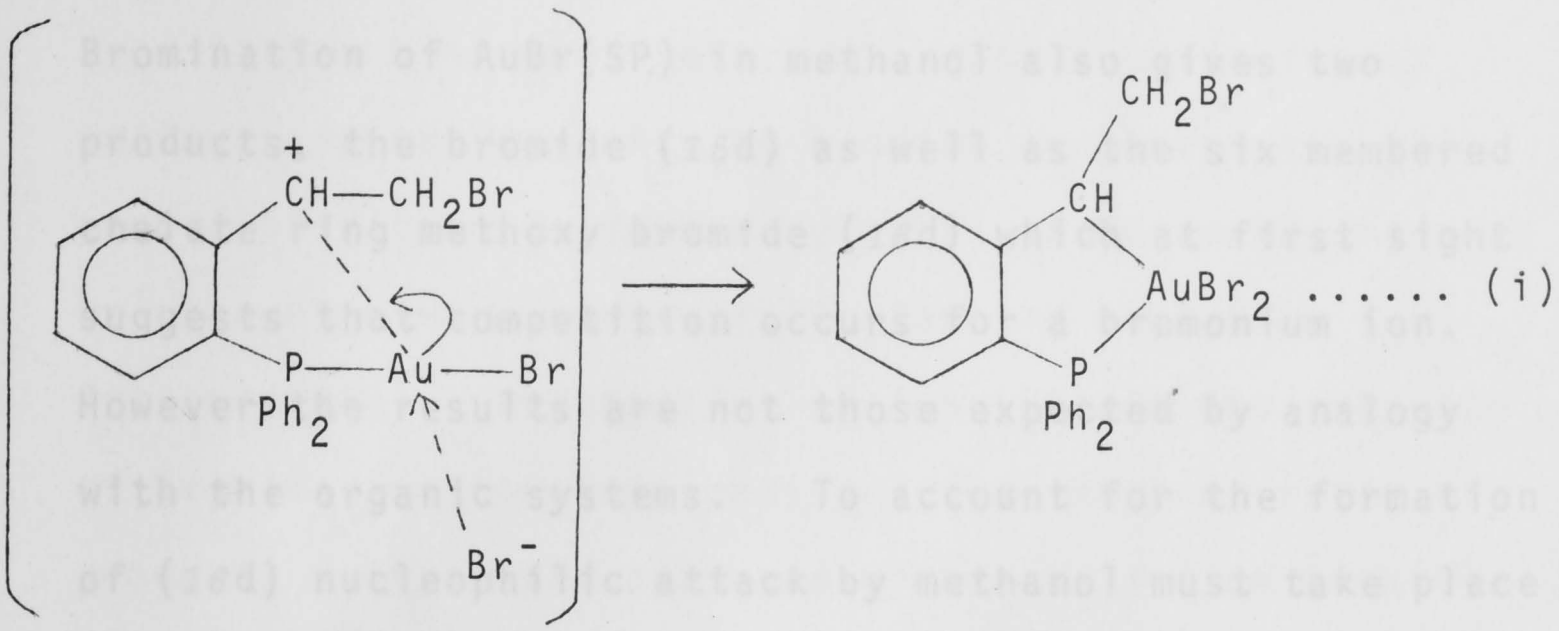
	Reagents	Solvent	Time	Result and ratio of products
1.	AuBr(SP), 0.1g., 0.000177mole Br_2, 0.028g., 0.000177mole	benzene 20ml	15 min	$AuBr_3$(SP) only
2.	AuBr(SP), 0.1g., 0.000177mole Br_2, 0.028g., 0.000177mole	methanol 30ml	15 min	Pale yellow/green solid Intermediate I . 1.33 $AuBr_3$(SP) . 1 $AuBr_2(SPOCH_3)$. 1
3.	AuBr(SP), 0.1g., 0.000177mole Br_2, 0.028g., 0.000177mole	methanol 30ml	1h	Pale yellow/green solid Intermediate I . 1 $AuBr_3$(SP) . 1 $AuBr_2(SPOCH_3)$. 1

TABLE III (continued)

4.	AuBr(SP), 0.1g., 0.000177mole Br_2, 0.028g., 0.000177mole	methanol 30 ml	3h	Brown/yellow solid $AuBr_3$(SP) . 1 $AuBr_2(SPOCH_3)$. 1 also unidentified product having $\tau(CDCl_3)$ 5.1 (d), 6.2-6.7 (m).
5.	AuBr(SP), 0.1g., 0.000177mole Br_2, 0.028g., 0.000177mole	benzene 2ml methanol 12ml	15 min	Orange solid Intermediate I . 1.5 $AuBr_3$(SP) . 1 $AuBr_2(SPOCH_3)$. 1
6.	AuBr(SP), 0.1g., 0.000177mole Br_2, 0.028g., 0.000177mole NaBr, 0.018g., 0.000177mole	benzene 2ml methanol 12ml	15 min	Yellow solid Intermediate I . 1.5 $AuBr_3$(SP) . 1 $AuBr_2(SPOCH_3)$. 1
7.	AuBr(SP), 0.1g., 0.000177mole Br_2, 0.028g., 0.000177mole NaBr, 0.18g., 0.00177mole	benzene 2ml methanol 12ml	15 min	Yellow solid Intermediate . 5 $AuBr_3$(SP) . 1 $AuBr_2(SPOCH_3)$. 1
8.	AuBr(SP), 0.1g., 0.000177mole Br_2, 0.028g., 0.000177mole	water 100ml	5 min	$AuBr_3$(SP) only.

TABLE III (continued)

9.	AuBr(SP), 0.1g., 0.000177mole Br_2, 0.028g., 0.000177mole KBr, 0.031g., 0.00026mole	water 100 ml	1 week	Pale yellow solid AuBr(SP) only.
10.	AuBr(SP), 0.1g., 0.000177mole Br_2, 0.028g., 0.000177mole NaBr, 0.07g., 0.0007mole	water 50ml	1½h	Yellow solid compound IV and $AuBr_3$(SP)
11.	AuBr(SP) 0.1g., 0.000177mole Br_2, 0.028g., 0.000177mole NaBr, 0.18g., 0.00177mole	methanol 30ml	3h	Yellow solid $AuBr_3$(SP) . 1 $AuBr_2(SPOCH_3)$. 1 also unidentified product having $\tau(CDCl_3)$ 4.3 (m), 4.8-4.9 (m).



A (15d)

Reaction (i) is unexpected as it implies that the gold atom in A is more susceptible to nucleophilic attack by Br^- than the secondary carbonium ion $-\overset{+}{C}H-$, a centre which would normally undergo nucleophilic attack readily.

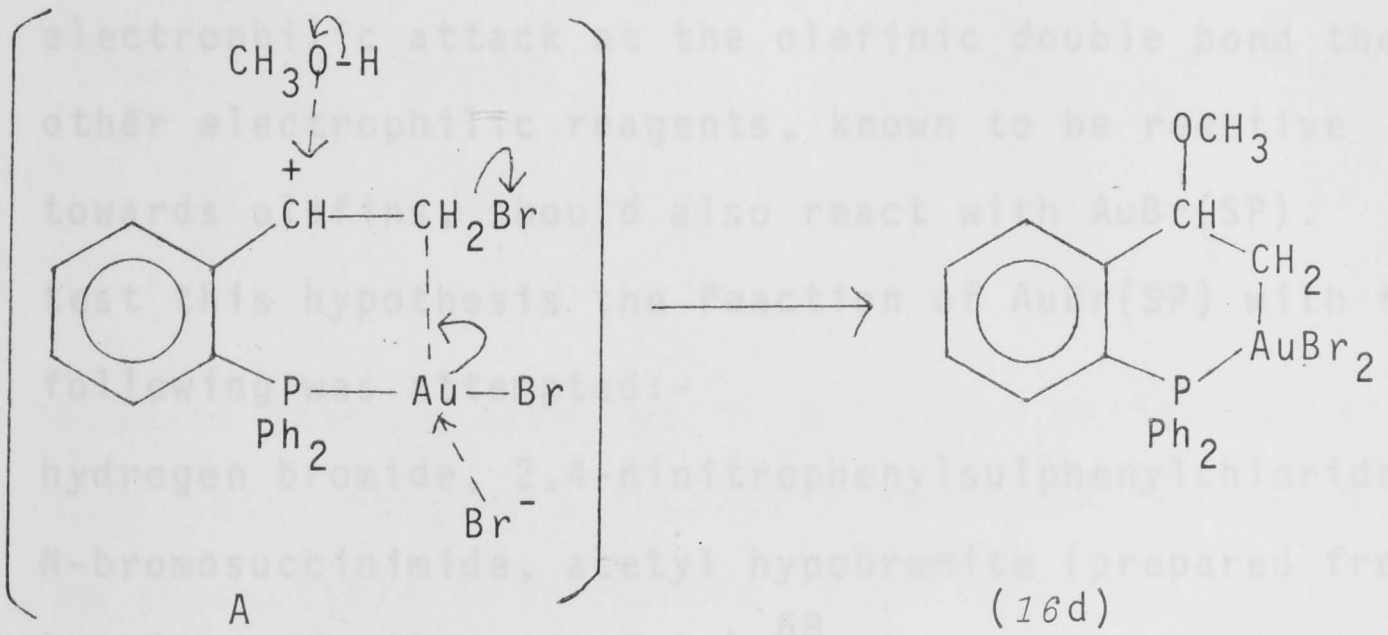
To see if a bromonium ion of type A is a possible intermediate the bromination of AuBr(SP) was carried out in methanol (see experiments 2-7). It has been found that bromination of stilbene in methanol gives two products,[67] stilbene methoxy bromide and stilbene dibromide. This indicates that a bromonium ion is formed by initial attack of Br^+, then competition occurs between methanol and Br^- in a second stage to give two products.

$$C_6H_5CH = CHC_6H_5 + Br_2 \longrightarrow C_6H_5CHBr\text{-}\overset{+}{C}HC_6H_5 + Br^-$$

Br^- (from the intermediate) → $C_6H_5CHBr\text{-}CHBrC_6H_5$

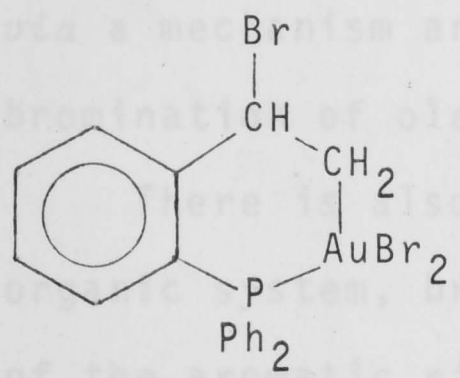
CH_3OH (from the intermediate) → $C_6H_5CHBr\text{-}CH(OCH_3)C_6H_5 + H^+$

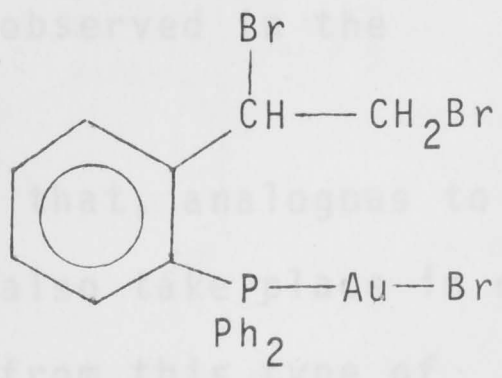
Bromination of AuBr(SP) in methanol also gives two products, the bromide (*15*d) as well as the six membered chelate ring methoxy bromide (*16*d) which at first sight suggests that competition occurs for a bromonium ion. However the results are not those expected by analogy with the organic systems. To account for the formation of (*16*d) nucleophilic attack by methanol must take place at the secondary carbonium ion in A at the same time as attack by Br^- at the gold atom.



A (*16*d)

In this case it is difficult to see why attack by Br^- does not also take place at the secondary carbonium ion to give one of the following products.





It has also been reported[67] that bromination of stilbene in the presence of bromide ion increases the amount of dibromide formed relative to methoxybromide as Br^- competes more successfully for the bromonium ion intermediate. Bromination of AuBr(SP) in the presence of bromide ion however seems to give the same ratio of products even in the presence of excess sodium bromide (see reactions 5, 6 and 7).

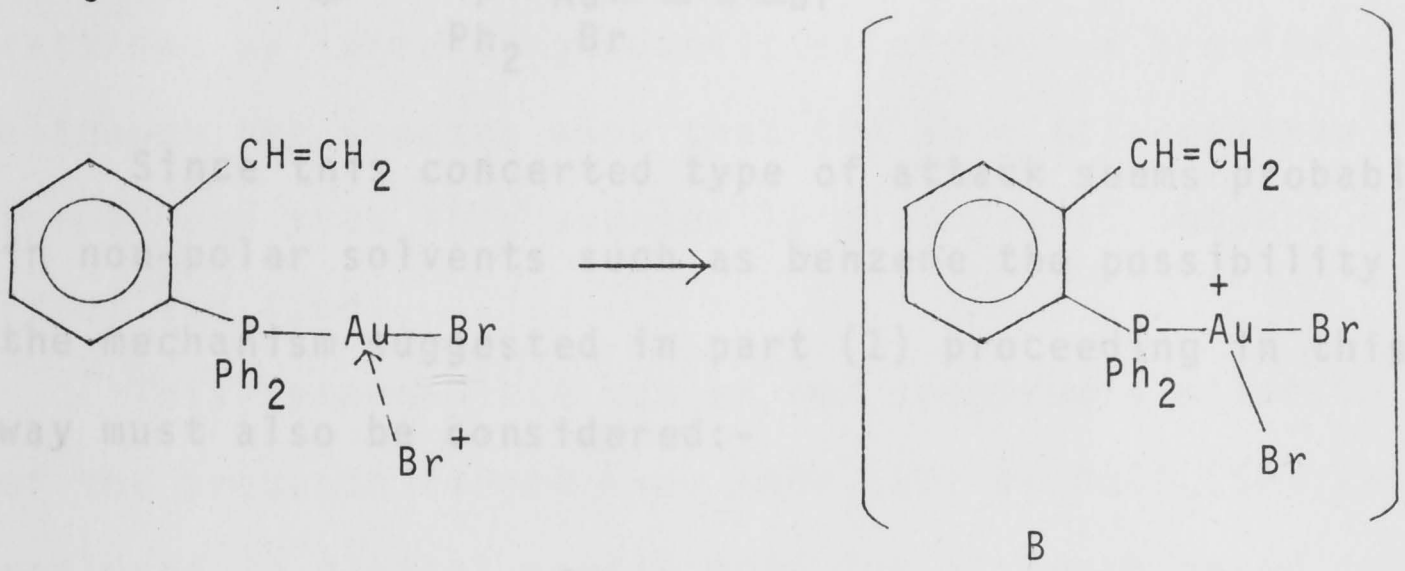
If bromination of AuBr(SP) proceeds *via* electrophilic attack at the olefinic double bond then other electrophilic reagents, known to be reactive towards olefins, should also react with AuBr(SP). To test this hypothesis the reaction of AuBr(SP) with the following was attempted:- hydrogen bromide, 2,4-dinitrophenylsulphenylchloride, N-bromosuccinimide, acetyl hypobromite (prepared from bromine and silver acetate).[68]

However, as summarised in Table VIII no reaction was detected between AuBr(SP) and any of these reagents. Therefore it appears unlikely that bromination proceeds *via* a mechanism analogous to that observed in the bromination of olefins.

There is also the possibility that, analogous to an organic system, bromination could also take place in one of the aromatic rings. Products from this type of reaction however have never been detected in any of these reactions.

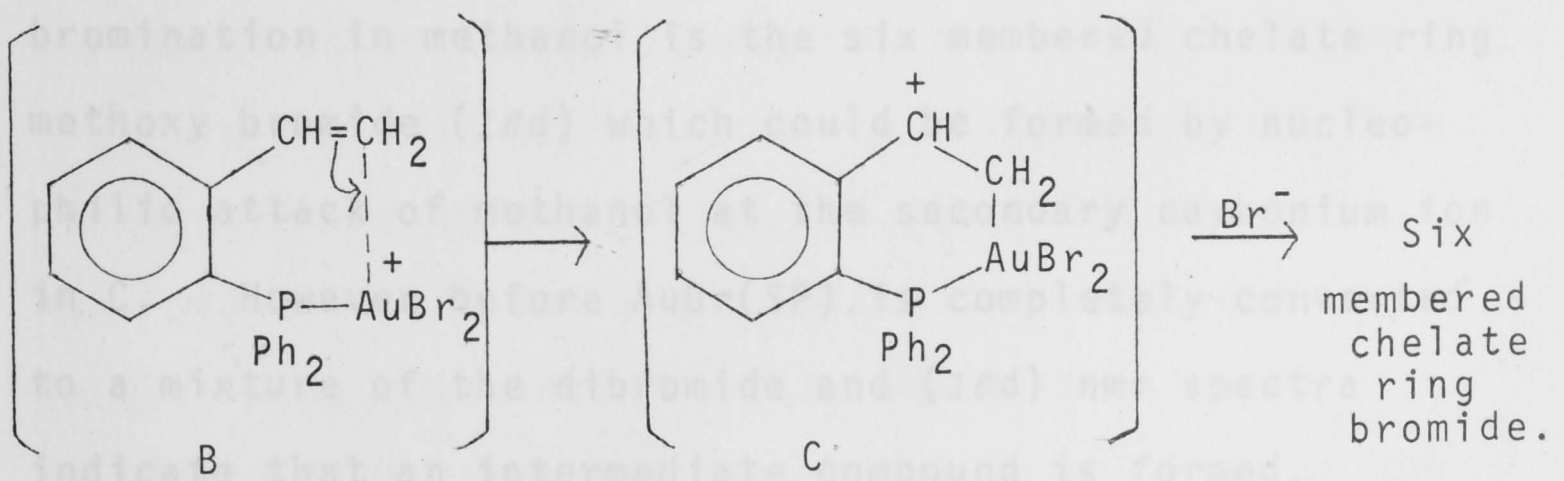
(2) Oxidative-addition

The bromination of AuBr(SP) can also be compared with the oxidative-addition of halogens to planar metal complexes[16] (see Chapter I). In this type of reaction electrophilic attack by Br^+ could take place at the metal to give the transition state B.



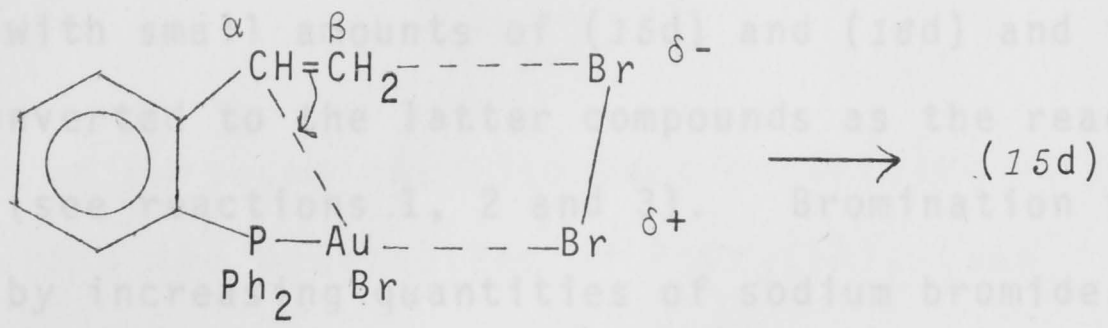
B

B would then be expected to rearrange as follows to give C. This contains a secondary carbonium ion which would be susceptible to nucleophilic attack, *e.g.* by Br^-, giving a six membered chelate ring complex.



To explain the formation of a five membered chelate ring complex one must assume that bromination proceeds *via* a concerted attack by a bromine molecule. Attack by Br^-

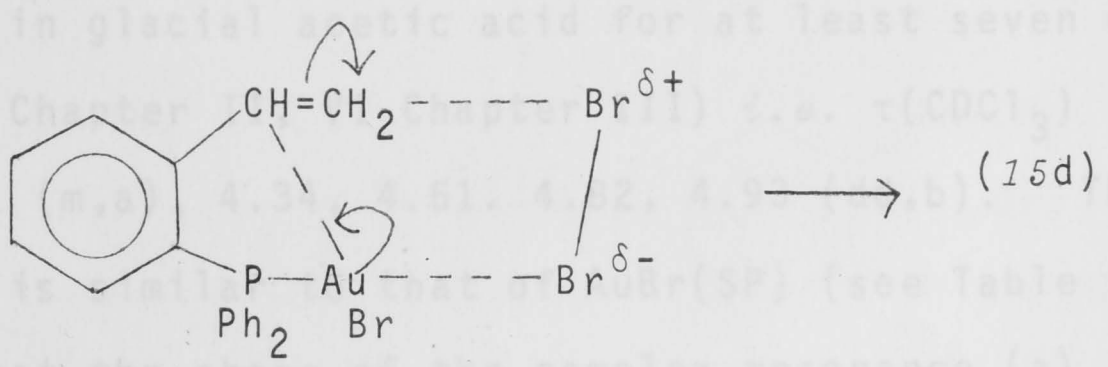
would then take place at the β-carbon atom in preference to the α-carbon atom for steric reasons.



(15d)

Since this concerted type of attack seems probable in non-polar solvents such as benzene the possibility of the mechanism suggested in part (1) proceeding in this way must also be considered:-

i.e.



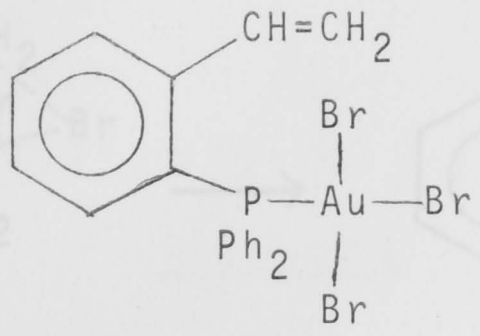
(15d)

As explained previously one of the products of bromination in methanol is the six membered chelate ring methoxy bromide (16d) which could be formed by nucleophilic attack of methanol at the secondary carbonium ion in C. However before AuBr(SP) is completely converted to a mixture of the dibromide and (16d) nmr spectra indicate that an intermediate compound is formed. Bromination of AuBr(SP) in methanol seems to be much slower than in benzene (see reactions 1, 2 and 5). Using the same quantities of reagents the reaction in

benzene takes fifteen minutes for completion while in methanol the same reaction takes three hours. An intermediate compound appears to be formed initially together with small amounts of (*15*d) and (*16*d) and is slowly converted to the latter compounds as the reaction proceeds (see reactions 1, 2 and 3). Bromination is also retarded by increasing quantities of sodium bromide, although nmr spectra show that the same intermediate is formed and that this eventually gives equal amounts of (*15*d) and (*16*d).

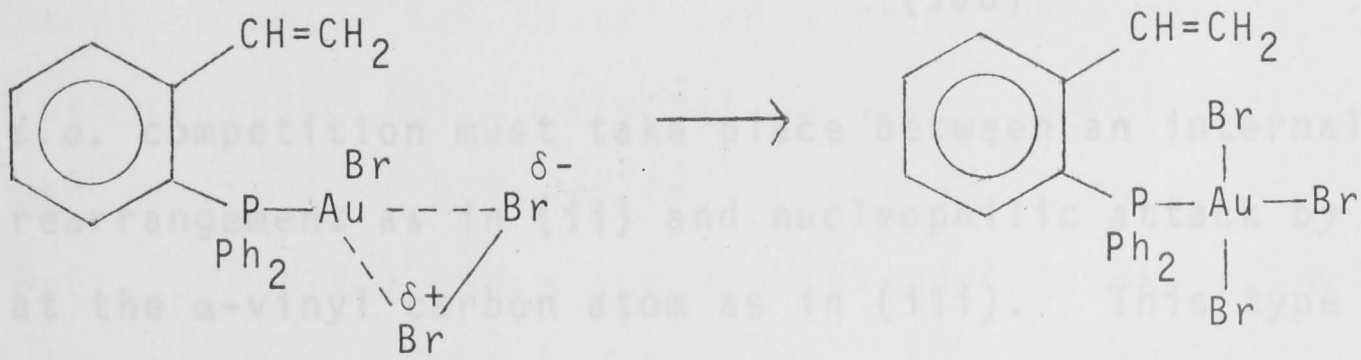
This intermediate has an nmr spectrum similar to one of the products formed when $AuBr_3$(SP) or $AuCl_3$(SP) is refluxed in glacial acetic acid for at least seven days, (see XIV Chapter II, VI Chapter III) *i.e.* $\tau(CDCl_3)$ 1.8 - 3.1 (m,a), 4.34, 4.51. 4.82, 4.93 (dd,b). This spectrum is similar to that of AuBr(SP) (see Table I) except that the shape of the complex resonance (a) is different from that observed in the same region in the nmr spectrum of AuBr(SP), and the two peaks at highest field in the pair of doublets are shifted upfield from those observed in AuBr(SP). (4.71τ and 4.82τ in AuBr(SP) to 4.82τ and 4.93τ in the intermediate). Therefore as postulated for XIV and VI this could also be a gold(III) complex in which the double bond of the ligand remains uncoordinated. (I).

(I)



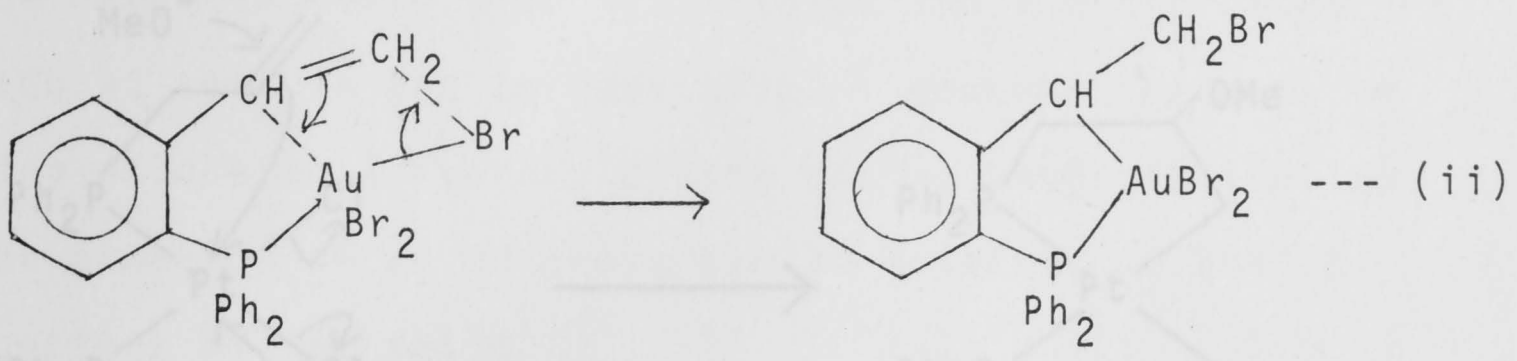
This type of compound has also been postulated as being formed during the bromination of $PtBr_2(SA)_2$ (see Chapter II, VI) and in the attempted bromination of AuBr(SA) (see IX, Chapter II).

If compound I is formed during the bromination in methanol, then it could be formed initially by oxidative-addition at the metal as shown.

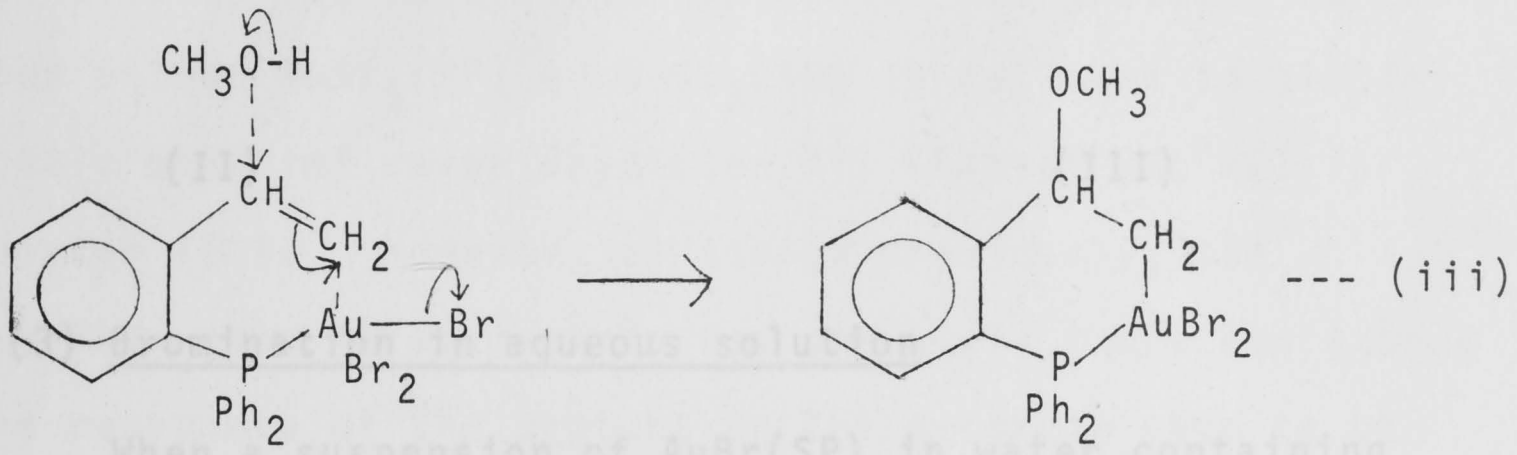


(I)

To account for the products formed when bromination is carried out in methanol reactions (ii) and (iii) must then take place simultaneously at approximately the same rate.



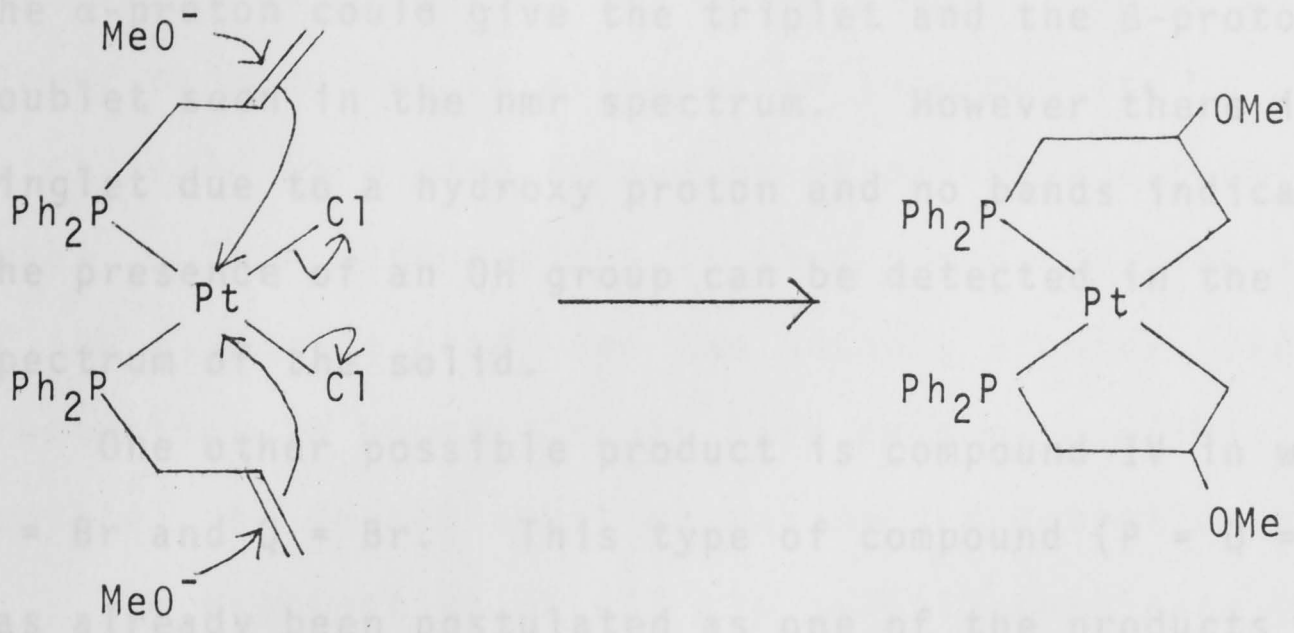
(15d) --- (ii)



(16d) --- (iii)

i.e. competition must take place between an internal rearrangement as in (ii) and nucleophilic attack by CH_3OH at the α-vinyl carbon atom as in (iii). This type of nucleophilic attack at an uncoordinated double bond, as in (iii), has been reported previously.[69]

cis-Bis(allyldiphenylphosphine)platinum(II) chloride (II) reacts with methoxide ion to give the σ-bonded complex (III) containing a five membered chelate ring. It is postulated that (III) is formed by a concerted reaction involving attack at the uncoordinated double bond as shown.

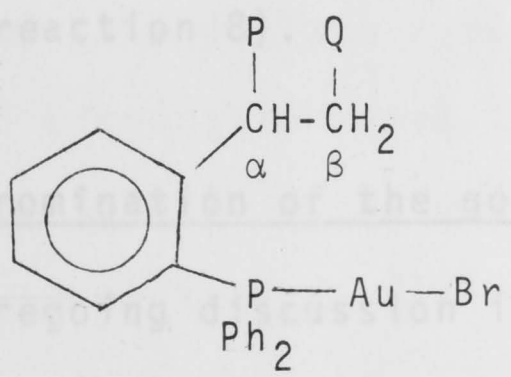


(II) (III)

(3) Bromination in aqueous solution

When a suspension of AuBr(SP) in water containing excess bromide ion is stirred with bromine for 1½ hours (see reaction 10) a pale yellow solid is obtained. The nmr spectrum of this solid shows that it contains $AuBr_3$(SP) (*15*d) and a compound IV having the following resonances:- τ($CDCl_3$) 3.56 (t,1, >C*H*-), 6.08 (d,2 -CH_2). Since aqueous bromination is a standard method for preparing olefin bromohydrins,[70] one would expect one product to be compound IV in which Q = Br and P = OH.

(IV)



The α-proton could give the triplet and the β-protons the doublet seen in the nmr spectrum. However there is no singlet due to a hydroxy proton and no bands indicating the presence of an OH group can be detected in the IR spectrum of the solid.

One other possible product is compound IV in which P = Br and Q = Br. This type of compound (P = Q = OAc) has already been postulated as one of the products formed when either $AuBr_3$(SP) or $AuCl_3$(SP) is refluxed in glacial acetic acid for seven days (see XV, Chapter II; VII in Chapter III). However, as stated previously, the α-carbon atom is asymmetric and one would therefore expect the resonance of the protons on the β-carbon atom to be more complex than the doublet observed. Also the formation of IV would require that addition took place at the double bond in preference to the gold atom which seems unlikely.

If a compound such as IV is formed then it is unstable as when the same reaction is carried out for one week (see reaction 9), the starting material only, AuBr(SP) is obtained. Also the presence of bromide ion seems necessary for its formation as bromination in water only gives $AuBr_3$(SP). (see reaction 8).

Summary of the bromination of the gold(I) complexes

From the foregoing discussion it appears that bromination of AuBr(SP) probably proceeds *via* initial

electrophilic attack at the metal atom. During the much slower bromination in methanol an intermediate is detected which could have been formed by oxidative-addition at the metal. This intermediate is then converted into a mixture of the dibromide (*15*d) and the methoxy bromide (*16*d). Bromination in benzene could also proceed *via* this intermediate, the faster reaction making its detection difficult.

The bromination of all the gold(I) complexes can be summarised as follows:-

(i) AuBr(SP) - in benzene gives the stable 5 membered chelate ring complex (*15*d). When brominated in methanol an intermediate, postulated as I, appears to be formed.

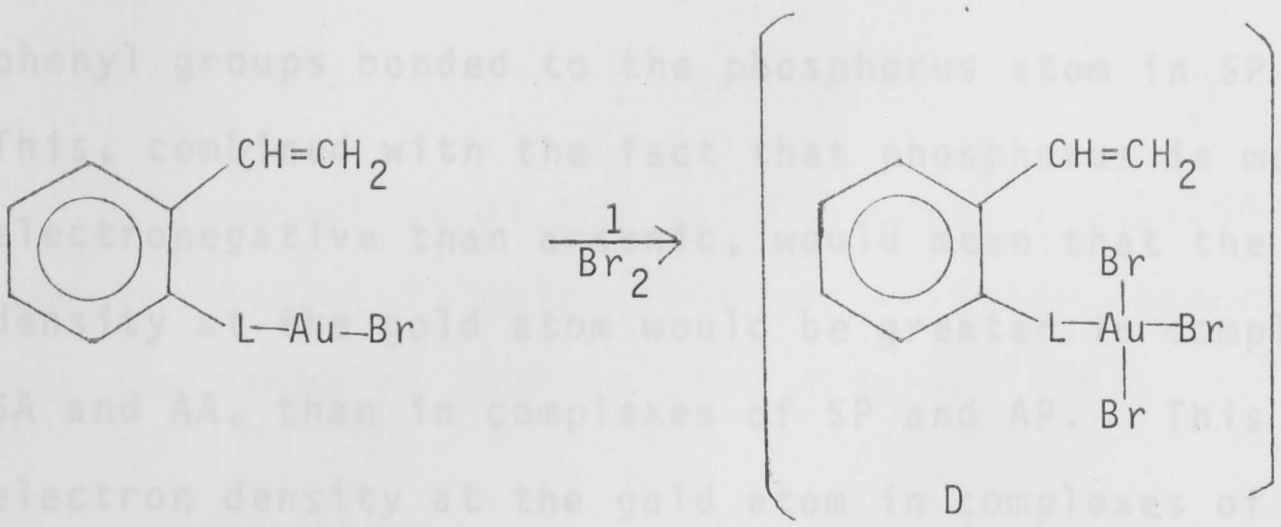
(ii) AuBr(SA) - does not give a chelate ring complex. Instead a complex similar to I is postulated as being formed. (see IX, Chapter II).

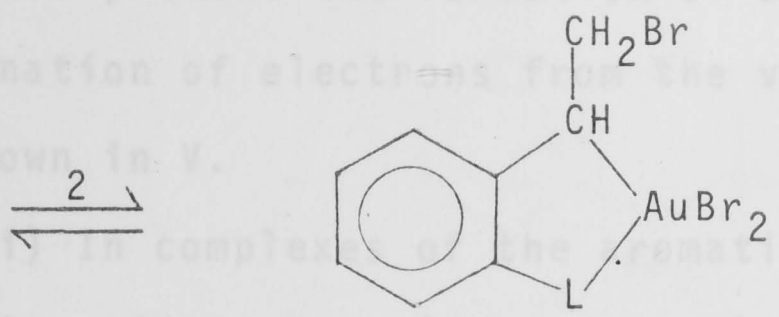
(iii) AuBr(AP) - gives a stable 6 membered chelate ring complex on bromination in benzene, $AuBr_3(AP)$.[39]

(iv) AuBr(AA) - gives a red solid of formula $AuBr_3(AA)$ thought to be a complex similar to I.[32]

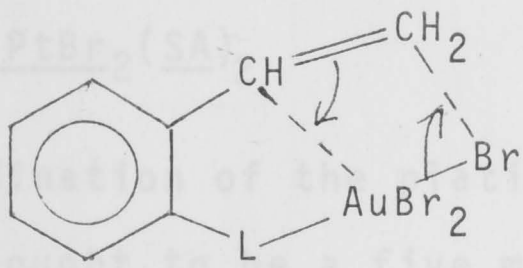
Therefore in the presence of an aromatic phosphorus donor ligand (SP and AP), stable complexes containing a gold-carbon σ-bond in a chelate ring are formed on bromination. If bromination does take place *via* the type of intermediate postulated as I, then the bromination reactions can be summarised as follows.

e.g. for the complexes of the styryl ligands. L = PPh_2, $AsMe_2$.





For the complexes of the methyl arsenic ligands it appears that reaction (1) only takes place, while reaction (2) proceeds in the complexes of the aromatic phosphorus ligands. For reaction (2) to take place the following mechanism has been postulated:-



(V)

Reaction (2) could fail to take place in the complexes of the methyl arsenic ligands for the following reasons:-

(i) Both arsenic ligands have two methyl groups bonded to the arsenic atom. These groups are known to have a much stronger electron releasing inductive effect than the phenyl groups bonded to the phosphorus atom.[71] This, combined with the fact that phosphorus is more electronegative than arsenic, would mean that the electron density at the gold atom would be greater in complexes of SA and AA, than in complexes of SP and AP. This high electron density at the gold atom in complexes of SA and AA could prevent the formation of a gold-carbon σ-bond by donation of electrons from the vinylic double bond, as shown in V.

(ii) In complexes of the aromatic phosphorus ligands, intermediate D could be unstable due to steric crowding at the gold atom caused by the presence of three bromine atoms and the two phenyl groups attached to the phosphorus atom. In the complexes of AA and SA however the smaller methyl groups attached to the arsenic atom would make D more stable, making the formation of the chelate complex less probable.

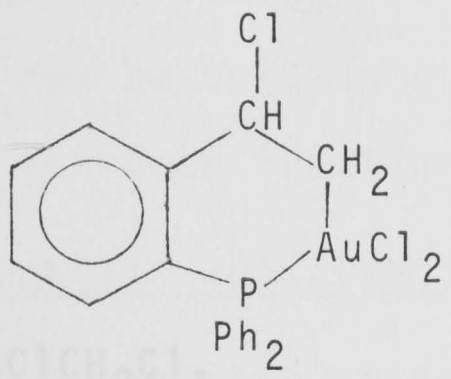
Bromination of $PtBr_2(SA)_2$

Since bromination of the platinum complex gives a product also thought to be a five membered chelate ring complex, it is assumed that the mechanisms postulated for the bromination of AuBr(SP) also apply to the platinum complex. In fact a complex similar to I has been postulated

as one of the bromination products of $PtBr_2(SA)_2$ (see Chapter II).

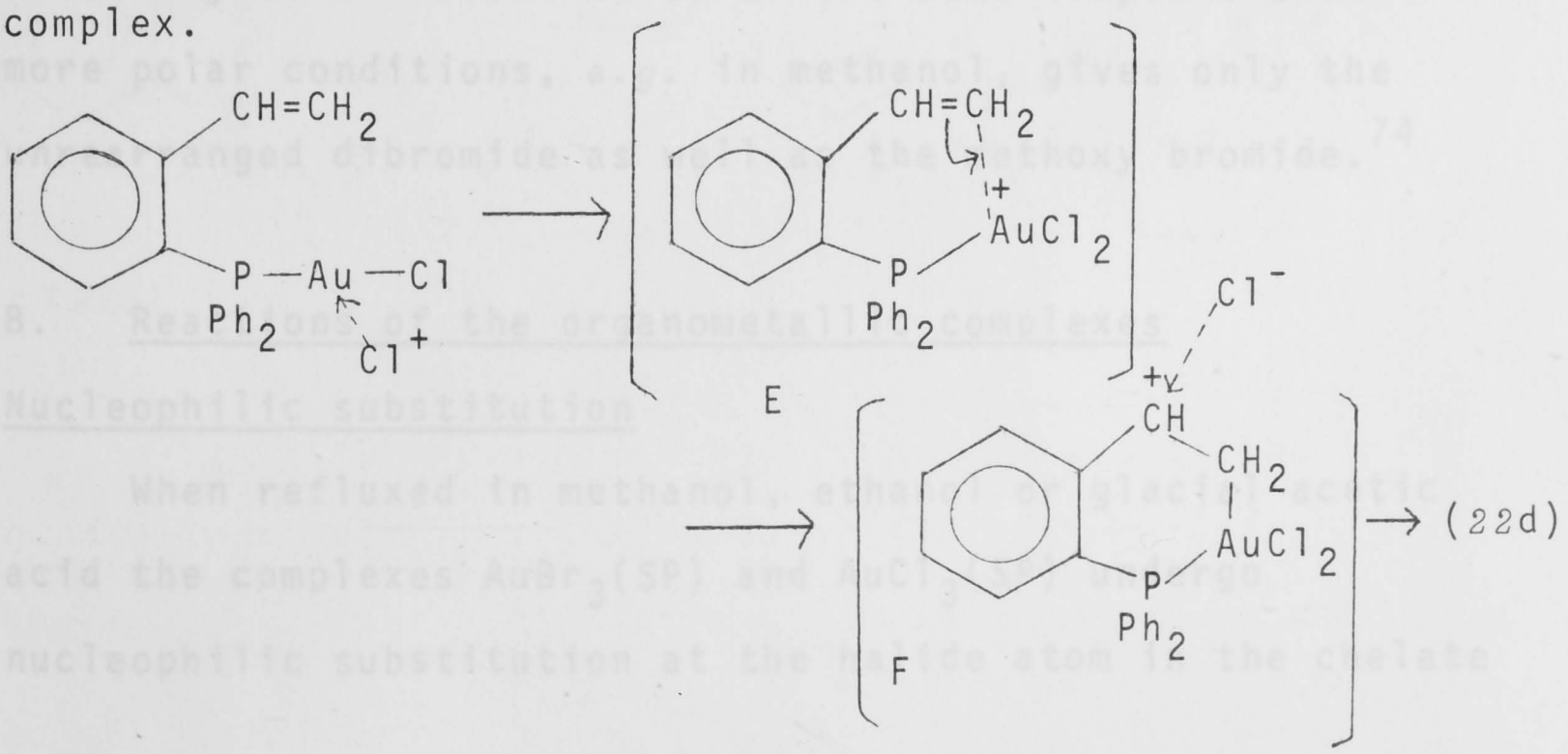
(ii) Chlorination

Chlorination of the gold(I) complex AuCl(SP) gives a complex $AuCl_3(SP)$ which from nmr evidence appears to be the six membered chelate ring complex (22d).

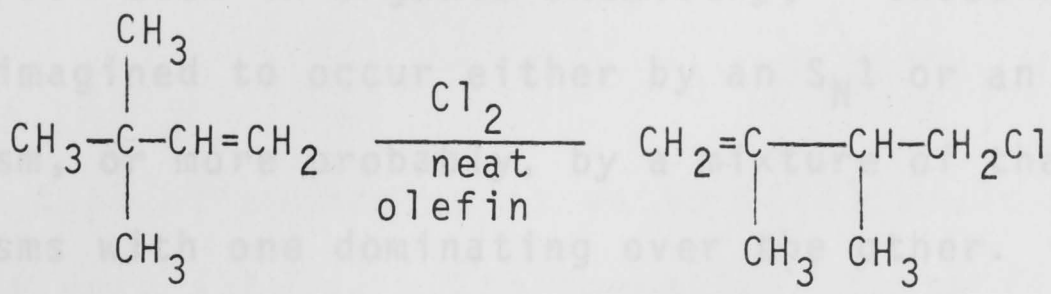


(22d)

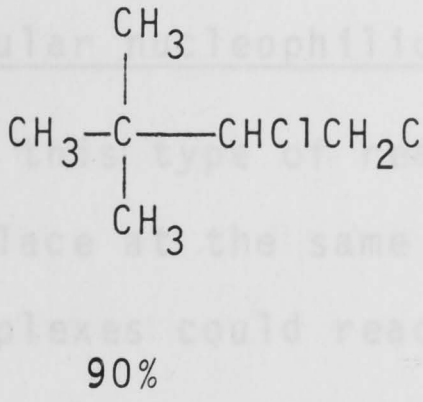
If chlorination, like bromination, involves initial electrophilic attack[72] at the metal then the reaction must proceed *via* formation of the intermediate E which then undergoes rearrangement to give F. Nucleophilic attack by Cl^- on F would give the six membered chelate ring complex.



It is worth noting for comparison that chlorination of double bonds in organic systems often gives a rearranged product. For example chlorination of *t*-butylethylene, even in non-polar solvents, gives 10% of a product formed by rearrangement of the olefin.[73]

i.e. 

10%

+ 

90%

This indicates the formation of a carbonium ion intermediate which can undergo rearrangement before nucleophilic attack by Cl^-. Bromination of the same compound under more polar conditions, *e.g.* in methanol, gives only the unrearranged dibromide as well as the methoxy bromide.[74]

B. Reactions of the organometallic complexes

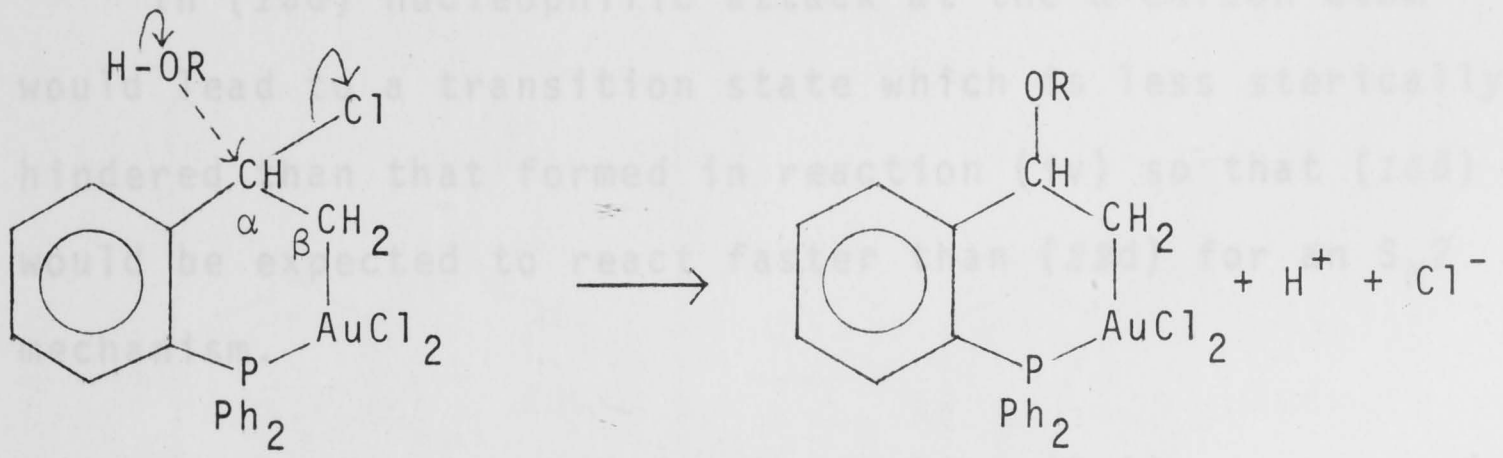
Nucleophilic substitution

When refluxed in methanol, ethanol or glacial acetic acid the complexes $AuBr_3$(SP) and $AuCl_3$(SP) undergo nucleophilic substitution at the halide atom in the chelate

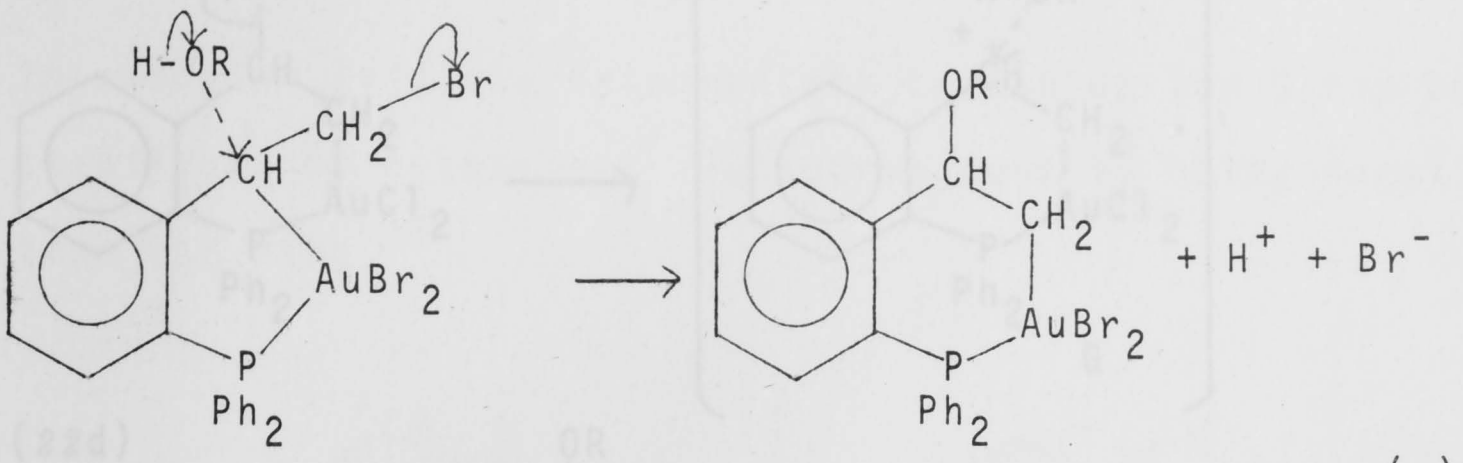
ring. (see Chapters II and III). Since it has been shown that the products are probably six membered chelate ring complexes, the bromide must undergo rearrangement from a five membered chelate ring complex during the course of the reactions. By analogy with nucleophilic substitution at a carbon atom in organic chemistry,[75] these reactions can be imagined to occur either by an S_N1 or an S_N2 mechanism, or more probably, by a mixture of the two mechanisms with one dominating over the other. Each type of mechanism will now be considered separately, then the most probable one for each reaction postulated.

Bimolecular nucleophilic substitution (S_N2).

In this type of reaction attack by the nucleophile takes place at the same time as removal of the halide ion. The complexes could react as follows:-



(22d) ------- (iv)



-------- (v)

(*15*d)

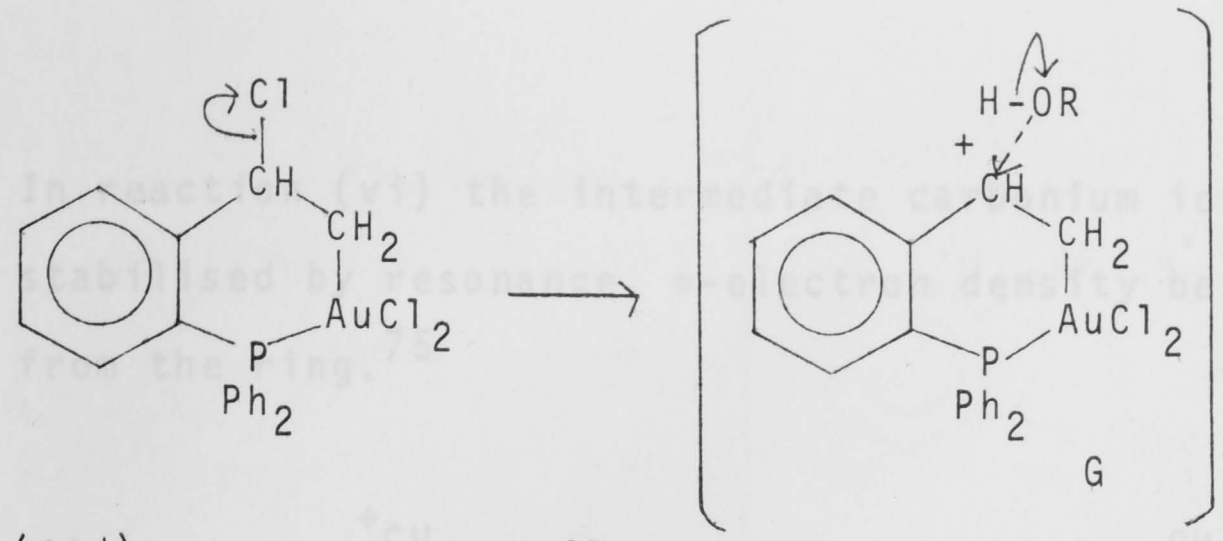
R = CH_3, C_2H_5, $COCH_3$

If this type of mechanism is valid (*22*d) would be expected to react very slowly. The formation of the five coordinate transition state would be greatly hindered as crowding would occur around the α-carbon atom. The chloride would also be expected to react more slowly than the bromide as the C-Cl bond is less easily distorted in the transition state than the C-Br bond due to differences in polarisability.[75]

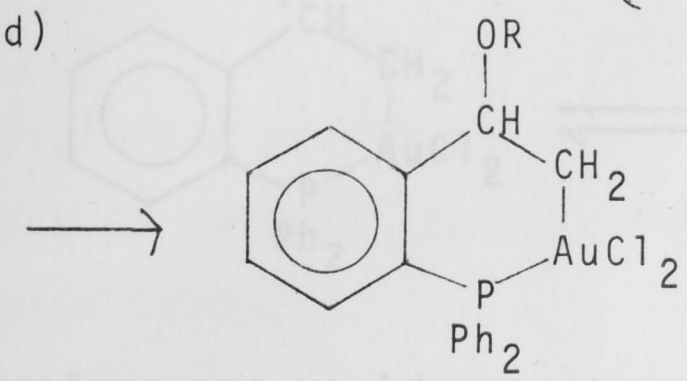
In (*15*d) nucleophilic attack at the α-carbon atom would lead to a transition state which is less sterically hindered than that formed in reaction (iv) so that (*15*d) would be expected to react faster than (*22*d) for an S_N2 mechanism.

<u>Unimolecular nucleophilic substitution</u> (S_N1).

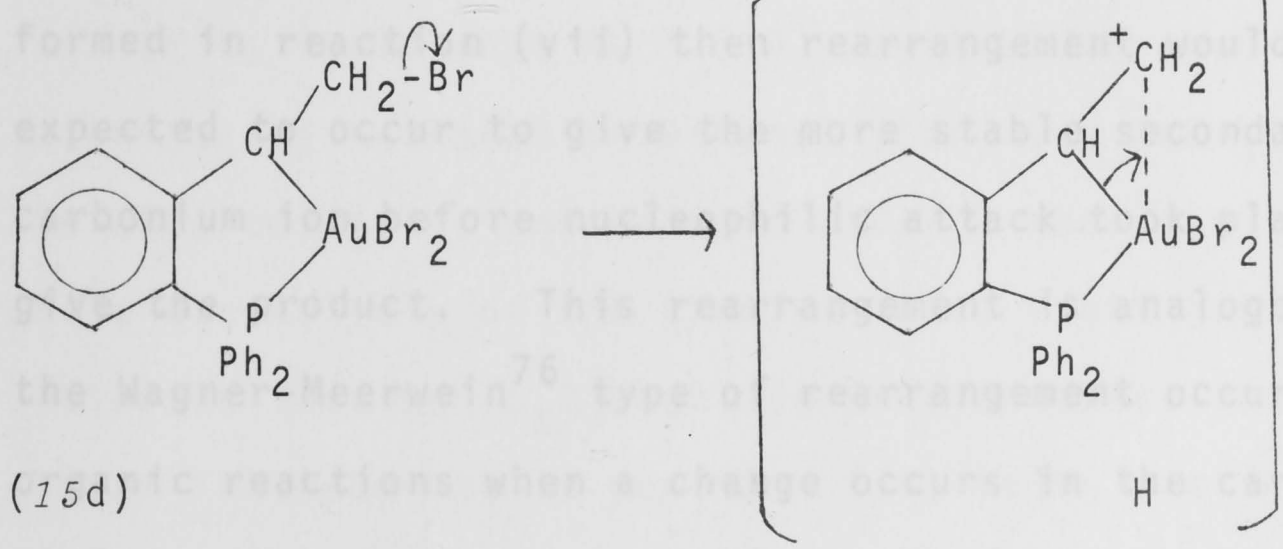
In an S_N1 reaction loss of a halide ion would occur first to give a carbonium ion intermediate. In this case the reactions could be imagined to take place as follows:-



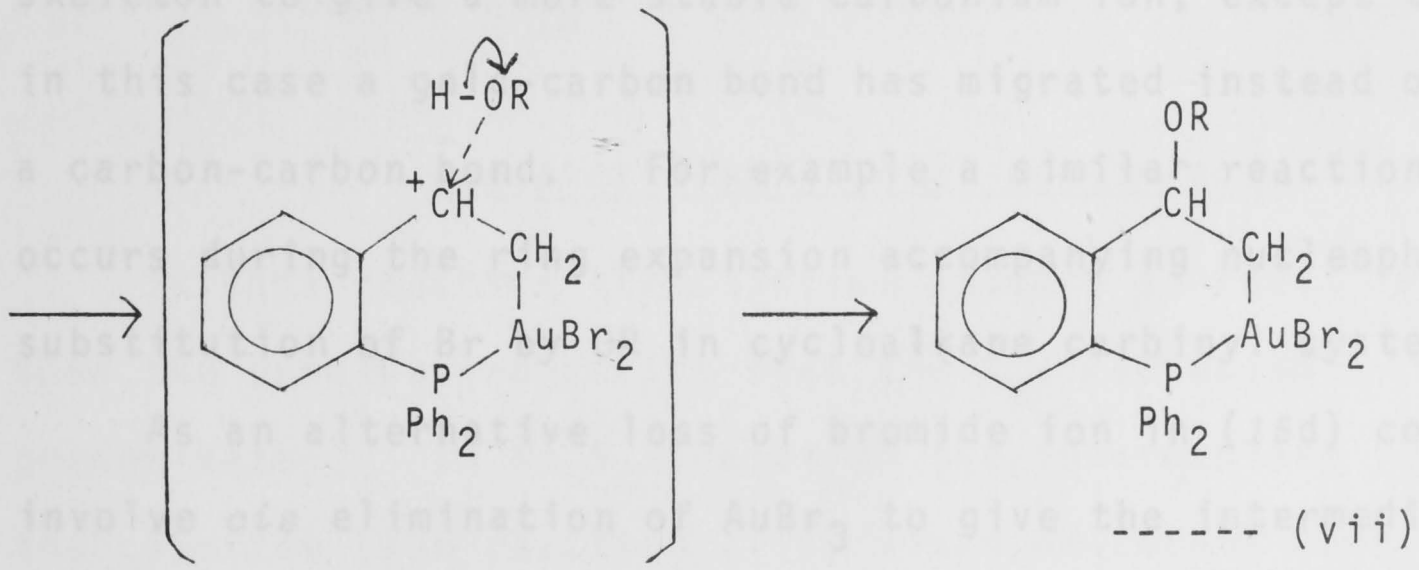
(22d)



----- (vi)

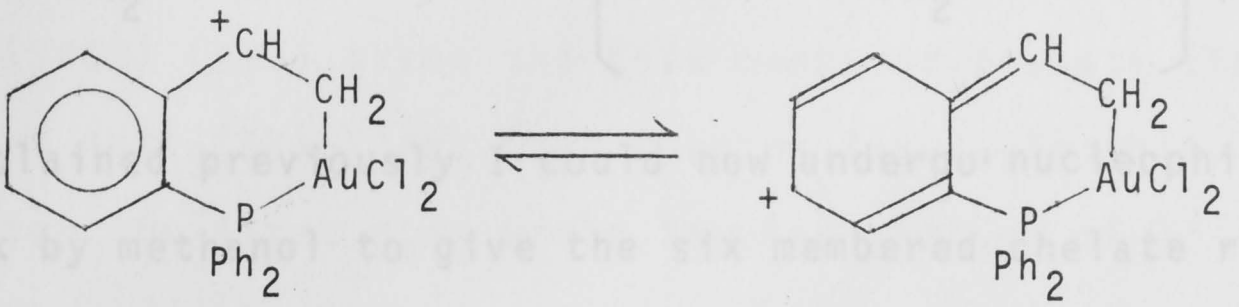


(15d)



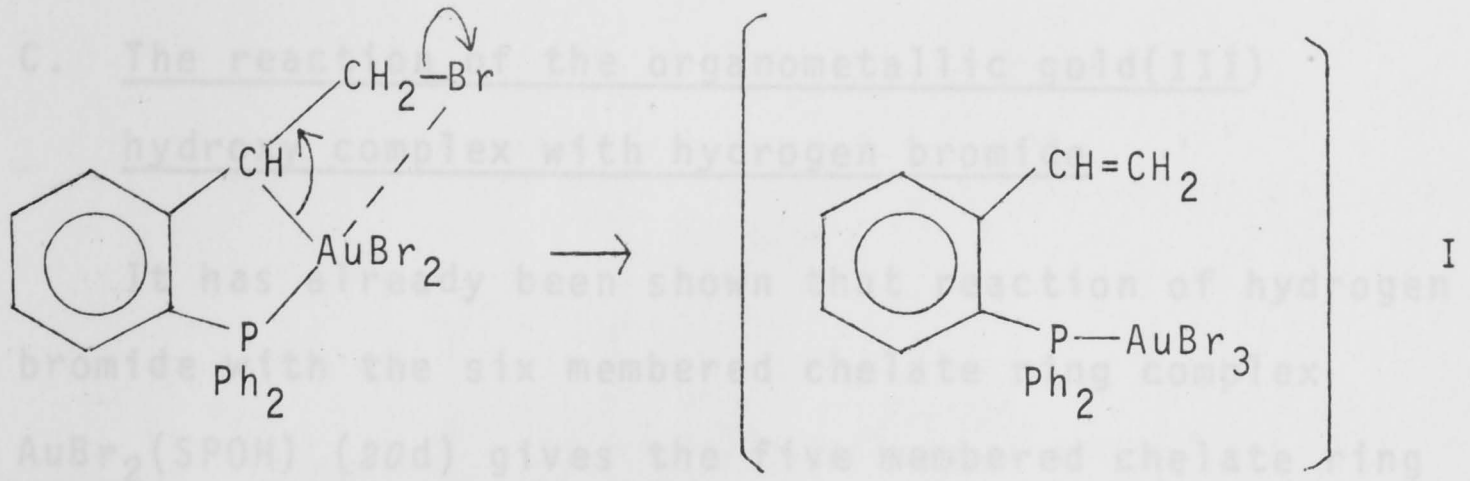
------ (vii)

In reaction (vi) the intermediate carbonium ion G may be stabilised by resonance, π-electron density being supplied from the ring.[75]



Therefore one would expect an S_N1 type of reaction on (22d) to be a relatively fast one. If intermediate H is formed in reaction (vii) then rearrangement would be expected to occur to give the more stable secondary carbonium ion before nucleophilic attack took place to give the product. This rearrangement is analogous to the Wagner-Meerwein[76] type of rearrangement occurring in organic reactions when a change occurs in the carbon skeleton to give a more stable carbonium ion, except that in this case a gold-carbon bond has migrated instead of a carbon-carbon bond. For example a similar reaction occurs during the ring expansion accompanying nucleophilic substitution of Br by OR in cycloalkane carbinyl systems.[77]

As an alternative loss of bromide ion in (15d) could involve *cis* elimination of $AuBr_3$ to give the intermediate I already postulated as being formed during the bromination of AuBr(SP) in methanol.



I

As explained previously I could now undergo nucleophilic attack by methanol to give the six membered chelate ring complex (22d).

Alcoholysis

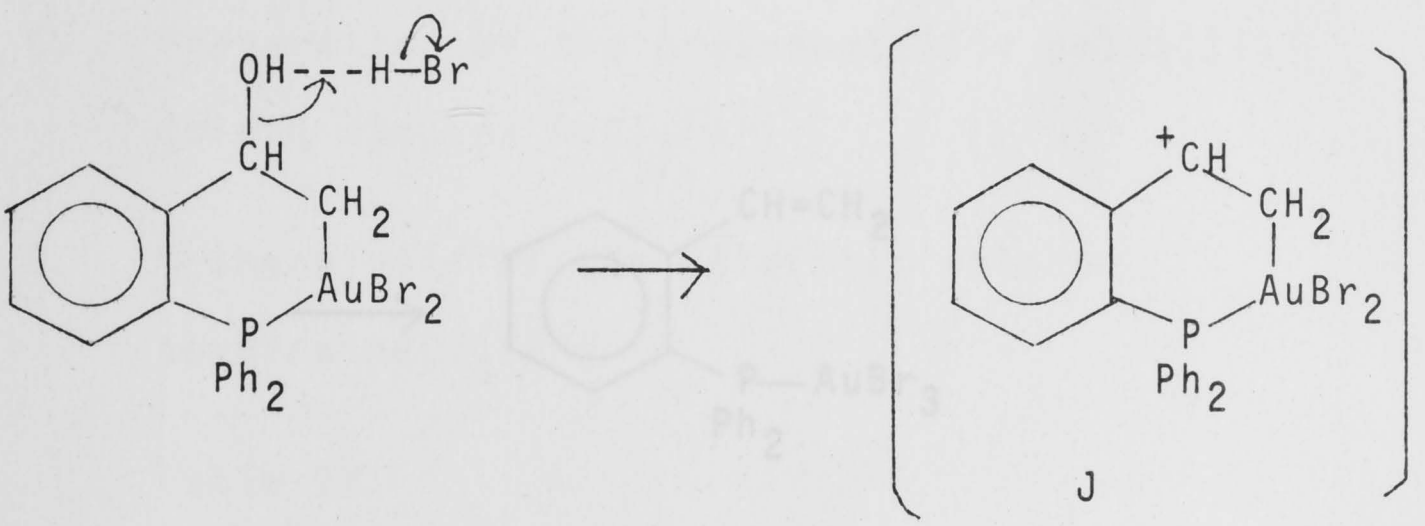
It is found that $AuCl_3$(SP) reacts much more slowly in refluxing methanol or ethanol than does $AuBr_3$(SP). The chloride takes one week to undergo complete reaction while alcoholysis of the bromide takes eight hours. This indicates that an S_N2 reaction predominates, the formation of the intermediate in reaction (iv) being sterically hindered compared with that in reaction (v).

Reaction with glacial acetic acid

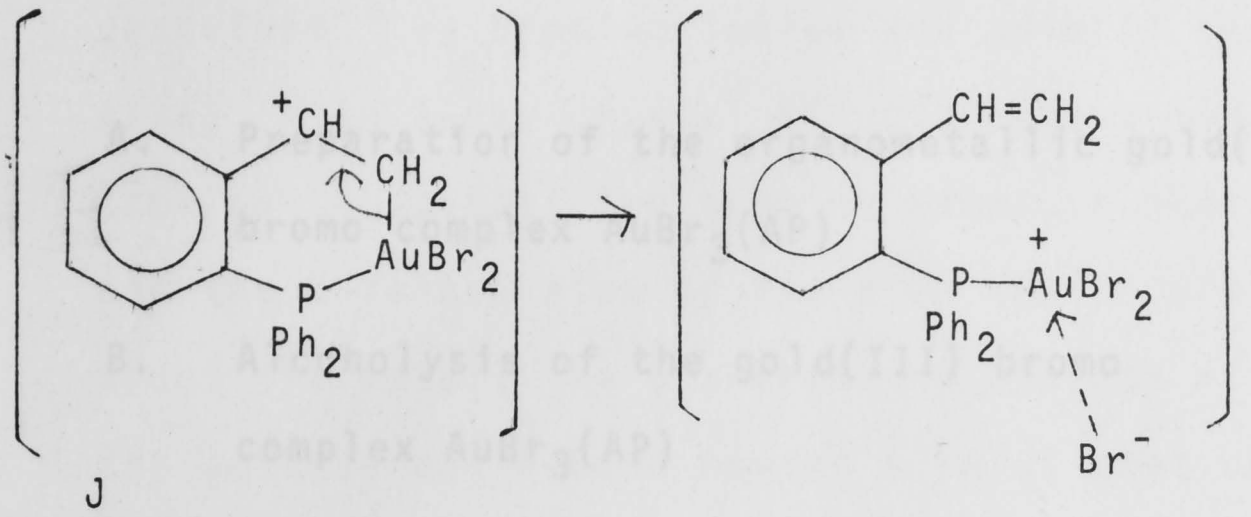
In this reaction the chloride appears to react faster than the bromide indicating that the S_N1 mechanism predominates. In an S_N1 reaction the intermediate for the chloride (see reaction (vi)) would be formed more readily than that for the bromide (reaction (vii)). In this reaction the S_N1 mechanism probably predominates because acetic acid is a more polar solvent than either methanol or ethanol.

C. <u>The reaction of the organometallic gold(III) hydroxy complex with hydrogen bromide</u>

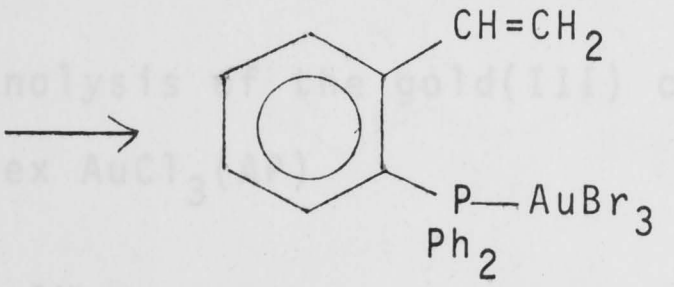
It has already been shown that reaction of hydrogen bromide with the six membered chelate ring complex $AuBr_2(SPOH)$ (*20*d) gives the five membered chelate ring complex $AuBr_3(SP)$ (*15*d) (see Chapter II). In this reaction the first step would involve removal of OH^- to give the intermediate J.



To explain the observed product this intermediate must now undergo rearrangement to give the gold(III) complex containing an uncoordinated double bond.



J



This compound, which is thought to be an intermediate formed during the bromination of AuBr(SP), must now undergo rearrangement to give (*15*d) (see page 119).

CHAPTER V

Organometallic gold(III) chloro and bromo compounds derived from the ligand *o*-allylphenyldiphenylphosphine

A. Preparation of the organometallic gold(III) bromo complex $AuBr_3(AP)$

B. Alcoholysis of the gold(III) bromo complex $AuBr_3(AP)$

C. Preparation of the organometallic gold(III) chloro complex $AuCl_3(AP)$

D. Methanolysis of the gold(III) chloro complex $AuCl_3(AP)$

Table IV.

Table V.

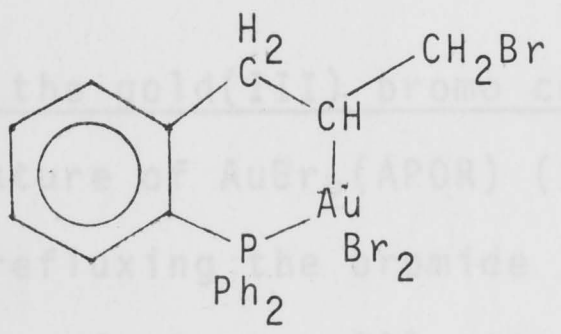
Table VI.

Nmr table VII.

A. Preparation of the organometallic gold(III) bromo complex $AuBr_3$(AP)

The complex $AuBr_3$(AP) (*15*a) is prepared as previously described[32] by bromination of the gold(I) complex AuBr(AP) (*12*a). An X-ray crystal structure determination[39] on the complex shows that two bromine atoms, a phosphorus atom, and the β-carbon atom of the side chain form a planar array about the metal, the six membered chelate ring containing the gold-carbon σ-bond having a twist boat conformation.

(*15*a)



The Au - Br distance *trans* to the σ-bonded carbon is significantly longer than that *trans* to phosphorus, a feature which has been observed previously in complexes containing transition metal-carbon σ-bonds, and which has been ascribed to the high σ-inductive electron donating effect of carbon as a ligand atom.[78]

The nmr spectrum of the chelate ring protons (see Table VII) is complex as expected for an AB_2C_2 system, the following being observed; τ($CDCl_3$) 5.26(m,2, -C*H*$_2$-), 6.38(m,1, >C*H*-), 6.75(m,2, -C*H*$_2$Br). These assignments however are very tentative for the following reasons:

(i) the assignment of the $-CH_2-$ and $-CH_2Br$ protons could be reversed,

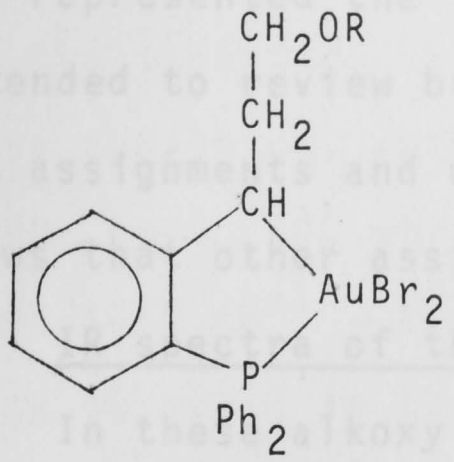
(ii) the complex resonance at 6.38τ could be due to one of the protons of the $-CH_2-$ group in the chelate ring. The resonance of the other methylene proton could be at 5.26τ together with a complex resonance due to the single proton >C*H*-. This is possible because by analogy with $AuBr_2(SPOCH_3)$ (*16*d) the two protons of the $-CH_2-$ group would be expected to have chemical shifts differing by approximately 67 Hz.

B. Alcoholysis of the gold(III) bromo complex $AuBr_3$(AP)

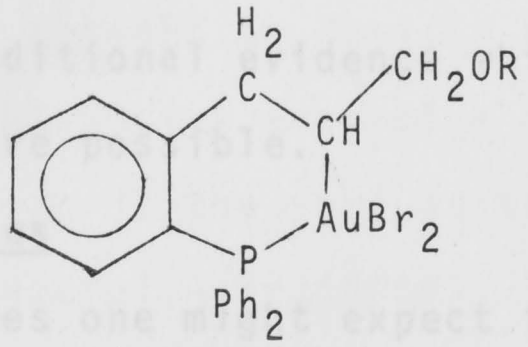
An isomeric mixture of $AuBr_2$(APOR) (R = CH_3, C_2H_5) can be prepared by refluxing the bromide (*15*a) in methanol or ethanol for thirty minutes. All attempts to obtain a pure sample of the more soluble isomer by fractional crystallisation as described by Kneen[32] were unsuccessful. Therefore an improved nmr spectrum of this isomer could not be obtained and no definite conclusions abouts its structure can be drawn. However nmr spectra of the pure less soluble isomer, and of a mixture containing mainly more soluble isomer, are better resolved than those obtained by Kneen. This enables more accurate integration of the spectra to be carried out although the resonances are still too complex to allow detailed assignments to be made.

Kneen proposed that (b) (see page 137) represented

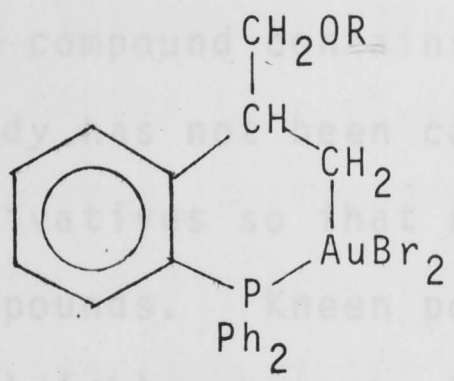
Structures postulated for the isomers of $AuBr_2(APOR)$



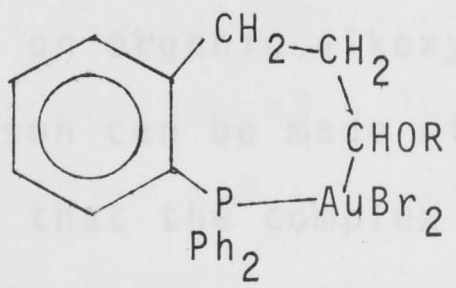
(a)



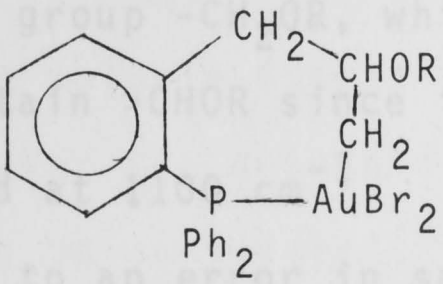
(b)



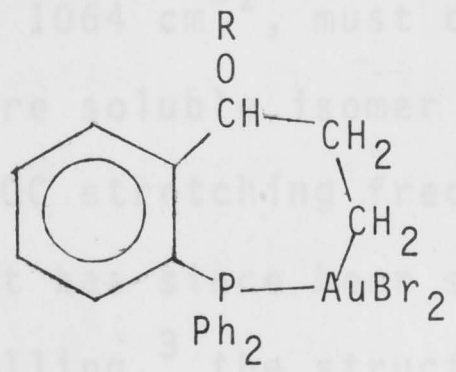
(c)



(d)



(e)



(f)

R = CH_3, C_2H_5

the structure of the more soluble isomer, while structure (c) represented the less soluble isomer. It is now intended to review briefly the evidence used by Kneen in his assignments and discuss additional evidence which shows that other assignments are possible.

(1) IR spectra of the complexes

In these alkoxy derivatives one might expect the exact position of the band due to a COC stretching[65] frequency, occurring in the region 1050 cm^{-1} - 1100 cm^{-1}, to depend on the structure of the compound, *i.e.* to indicate whether the compound contains $-CH_2OR$ or >CHOR. However a detailed study has not been carried out on organic alkoxy derivatives so that no comparison can be made with these compounds. Kneen pointed out that the complex $PtBr_3$(AAOEt)(AA) (*6*b), shown by X-ray studies to contain $-CH_2OEt$,[79] had strong COC stretching bands at 1077 cm^{-1} and 1060 cm^{-1}. He therefore suggested that the less soluble isomer, having a corresponding band at 1064 cm^{-1}, must contain the group $-CH_2OR$, while the more soluble isomer must contain >CHOR since it has a COC stretching frequency band at 1100 cm^{-1}. However it has since been shown that due to an error in sample labelling,[3] the structure determination was in fact carried out on the complex $PtBr_3$(SAOEt)(SA) (*6*c) containing the group >CHOR. Therefore it appears that the alkoxy bands in the two isomers must have the reverse assignment to that given above. However when a detailed study is made of all the gold and

platinum alkoxy derivatives it appears that there is no correlation between the frequency of the ν(COC) vibration and the structure of the alkoxy derivatives (see Table IV). These complexes, which are all thought to contain the group >CHOR, have COC stretching frequencies extending over the range 1080 cm^{-1} - 1110 cm^{-1} which is the same as the range observed in the two isomers of $AuBr_2$(APOR). Therefore no definite conclusions on the structure of the isomers can be drawn from their IR spectra.

(2) Nmr spectra of the complexes

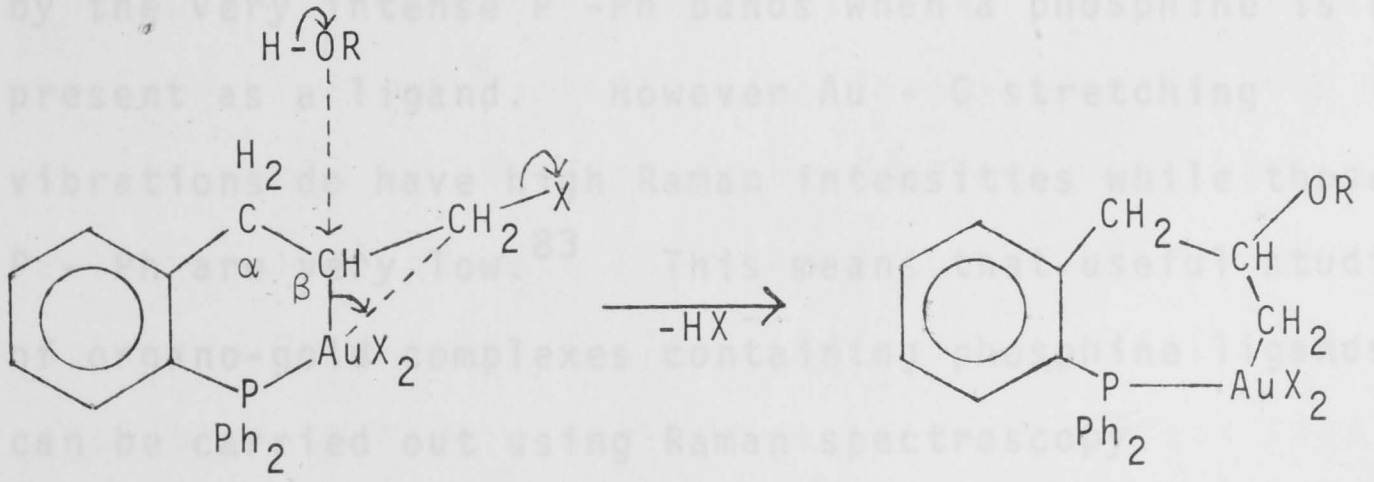
The nmr spectrum of the more soluble isomer of AuX_2(APOR) (X = Cl,Br; R = CH_3, C_2H_5) shows a complex resonance, corresponding to one proton, at a low field of 5.3τ - 5.6τ (see Table VII) which is not present in the nmr spectrum of the less soluble isomer. Kneen assigned this to >C*H*-Au and attributed the low τ-value to the deshielding effect of the σ-bonded gold(III) atom.[80] Two protons on a carbon atom adjacent to the gold atom would not be deshielded to the same extent. On this basis the more soluble isomer could have structures (a), (b) or (d). However the deshielding effect of the alkoxy group should also be considered,[81] as a single proton on a carbon atom adjacent to OCH_3 or OC_2H_5 would also be expected to give a low field resonance. In the gold(III) complexes derived from the ligand SP a comparison of this effect can be made which seems to indicate that the gold(III)

atom has a greater deshielding effect than the alkoxy group (see Table V). In the nmr spectra of the complexes $AuBr_3(AP)$ and $AuCl_3(AP)$ the exact position of the >C*H*- resonance is uncertain. The resonance could be at 6.38τ, or as low as 5.26τ. If the former is correct then the gold atom does not appear to have a strong deshielding effect in these complexes. Therefore the complex resonance at 5.6τ - 5.7τ in the alkoxy derivatives could be due to a single proton on a carbon atom adjacent to an alkoxy group, as in (d), (e) or (f), or it could be due to >C*H*- Au as in (a), (b) or (d).

Therefore again any assignments made from nmr spectroscopic evidence are very tentative.

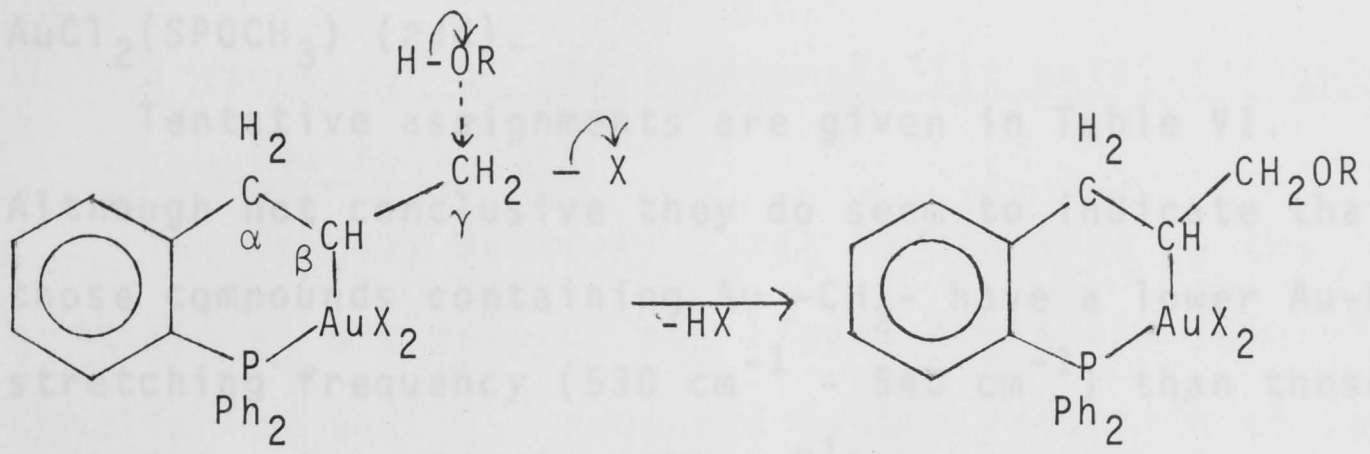
(3) Mechanisms for the formation of the alkoxy derivatives

By comparison with the mechanism postulated for the formation of $AuX_2(SPOR)$ (X = Br,Cl; R = CH_3, C_2H_5) in Chapter IV one would expect the following to take place during the alcoholysis of $AuBr_3(AP)$ or $AuCl_3(AP)$, giving the structure (e).



X = Cl, Br.

It is also possible that for steric reasons nucleophilic attack at the β-carbon atom is hindered in these complexes. Direct nucleophilic substitution could occur at the γ-carbon atom to give the structure (b).



X = Cl, Br.

Therefore on mechanistic considerations structures (b) and (e) seem probable.

(4) Raman spectra of the complexes

It has been reported that the IR intensities of the bands due to Au - C stretching frequencies in organo-gold compounds are usually very low.[80, 82] The bands occur in the region 450 cm^{-1} - 550 cm^{-1} where they are masked by the very intense P -Ph bands when a phosphine is also present as a ligand. However Au - C stretching vibrations do have high Raman intensities while those of P - Ph are very low.[83] This means that useful studies of organo-gold complexes containing phosphine ligands can be carried out using Raman spectroscopy.

In these studies reasonable Raman spectra could only be obtained of the following compounds, and these include

the chloro complexes derived from the ligand AP which are discussed later.

$AuBr(SP)$ (*12*d), $AuBr_3(SP)$ (*15*d), $AuBr_2(SPOCH_3)$ (*16*d), $AuCl(AP)$ (*13*a), $AuCl_3(AP)$ (*22*a), $AuCl_2(APOCH_3)$ (*24*a) - less soluble isomer,

$AuCl_2(SPOCH_3)$ (*24*d).

Tentative assignments are given in Table VI. Although not conclusive they do seem to indicate that those compounds containing Au $-CH_2-$ have a lower Au-C stretching frequency (530 cm^{-1} - 540 cm^{-1}) than those containing Au - CH< (*ca* 570 cm^{-1}). If this is correct then the less soluble isomer of $AuCl_2(APOCH_3)$, which from nmr spectra appears to have the same structure as $AuBr_2(APOCH_3)$, would have structure (c), (e) or (f), its Raman spectrum having a Au - C stretching frequency band at 540 cm^{-1}.

Summary of evidence

Although Kneen made reasonable assignments for the structures of the two isomers on the evidence he had available it now appears that other structures are possible. On mechanistic considerations only, the two isomers would be expected to have structures (b) and (e). Raman spectra indicate that the less soluble isomer contains $-CH_2-Au$, as in (e), while if gold(III) is considered to have a greater deshielding effect than the alkoxy group, nmr spectra indicate that the more soluble isomer contains >CH-Au, as in (b).

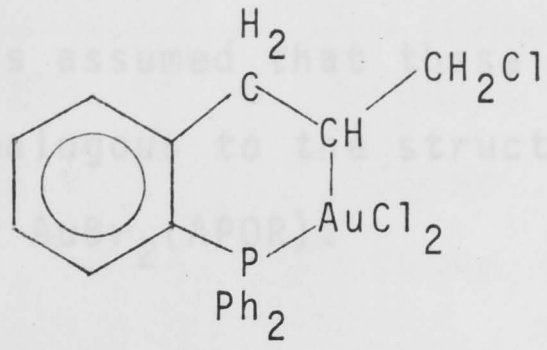
Therefore although this additional evidence seems to support Kneen's assignment for the structure of the more soluble isomer, the possibility of another structure for the less soluble isomer must also be considered.

C. Preparation of the organometallic gold(III) chloro complex $AuCl_3$(AP)

The complex AuCl(AP) (*13*a) is prepared by the addition of one mole of the ligand AP to one mole of the complex ion $[AuCl_2]^-$ prepared by the reduction of sodium tetrachloroaurate(III) with sodium metabisulphite in the presence of excess lithium chloride. It is a colourless crystalline compound the IR spectrum of which shows a band at 1640 cm^{-1} due to a C=C stretching frequency indicating that the double bond in the ligand is uncoordinated.[36]

Treatment of AuCl(AP) with chlorine in benzene gives a yellow crystalline solid analysing as $AuCl_3$(AP). The nmr spectrum of this solid (see Table VII) is very similar to that of $AuBr_3$(AP), therefore it is assumed that this too is a gold(III) complex having a Au-C σ-bond in a six membered chelate ring (*22*a). The IR spectrum of the complex shows no bands assignable to an uncoordinated double bond, instead new bands appear at 720 cm^{-1} and 760 cm^{-1} which could be due to C-Cl stretching frequencies.[62]

(22a)



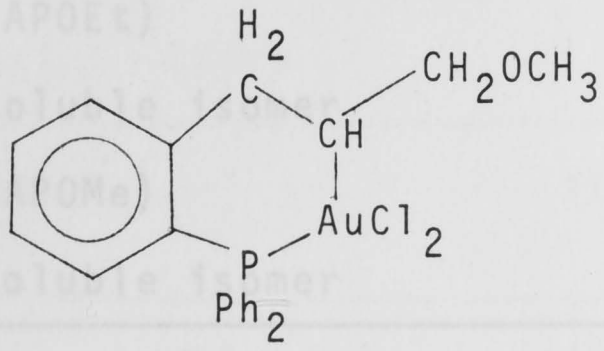
This suggests that unlike the corresponding trihalides in the complexes derived from SP, (15d) and (22d), the complexes $AuBr_3$(AP) and $AuCl_3$(AP) have the same chelate ring structure indicating that they are formed by the same mechanism. This mechanism would probably be similar to that suggested for the formation of $AuBr_3$(SP) in Chapter IV.

D. Methanolysis of the gold(III) chloro complex $AuCl_3$(AP)

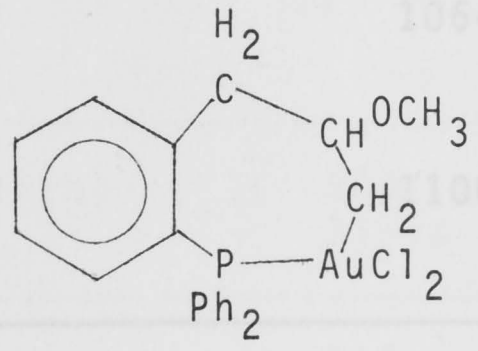
A mixture of two isomeric compounds analysing as $AuCl_2(APOCH_3)$ can be obtained by refluxing $AuCl_3$(AP) (22a) in methanol for six hours. This again indicates that (22a) contains the primary group $-CH_2Cl$ since alcoholysis of a secondary group >CHCl, as in a seven membered chelate ring complex, would be expected to be a much slower reaction. Alcoholysis of $AuCl_3$(SP) (which contains the group >CHCl) takes one week for completion. The isomeric compounds $AuCl_2(APOCH_3)$ (24a) have nmr spectra very similar to those of the isomers of $AuBr_2(APOCH_3)$ (see Table VII) and again

complete separation of the isomers is not possible. Therefore it is assumed that these isomers have structures (g) and (h) analogous to the structures (b) and (e) postulated for $AuBr_2$(APOR).

(*24*a)



(g)



(h)

more soluble isomer

less soluble isomer.

TABLE IV

Complex	Alkoxy group	COC band (cm^{-1})
$PtBr_3(SAOEt)(SA)$	>CHOEt	1077, 1060
$PtBr_3(SAOMe)(SA)$	>CHOMe	1080, 1060
$AuBr_2(SPOMe)$	>CHOMe	1100
$AuCl_2(SPOMe)$	>CHOMe	1110
$AuBr_2(SPOEt)$	>CHOEt	1110
$AuBr_2(APOEt)$ less soluble isomer	?	1064
$AuBr_2(APOMe)$ more soluble isomer	?	1100

TABLE V

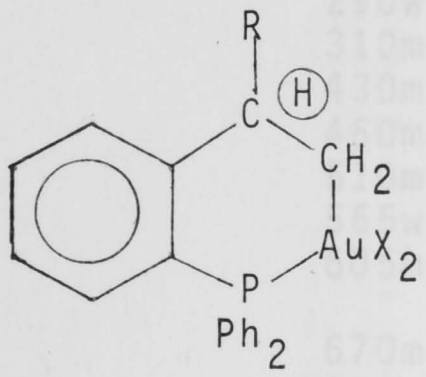
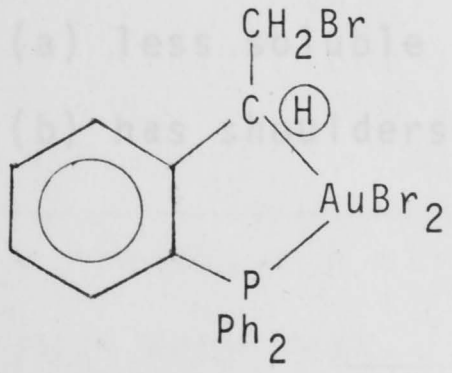
Complex	R	X	Ⓗ τ
	OCH_3	Br	4.61
	OH	Br	4.60
	$OCOCH_3$	Br	4.60
	OCH_3	Cl	4.87
	$OCOCH_3$	Cl	4.60
	Cl	Cl	4.73
	complex resonance at 4.40τ due to Ⓗ		

TABLE VI

Characteristic bands of the Raman spectra of the gold complexes (cm^{-1})

	$AuBr_2(SPOCH_3)$ thought to contain Au - CH_2	$AuCl_2(SPOCH_3)$ thought to contain Au - CH_2	$AuCl_2(APOCH_3)$ thought to contain Au - CH_2 (a)
ν(Au-Br)	205vs		
ν(Au-Cl)		310s (b)	280s 315vs
ν(Au-C)	530s	530m	540m
		Other bands	
		210m	205s
	245vw	225m	235m
	265m		
	290w		
	310m		
	430m	435m	440m
	460m	460m	475m
	510m		495m
	565w	575m-w	535m
	605m	610m	600w
			625m
	670m	675m	
	710w	720w	

(a) less soluble isomer

(b) has shoulders at 265, 270 and 285 cm^{-1}.

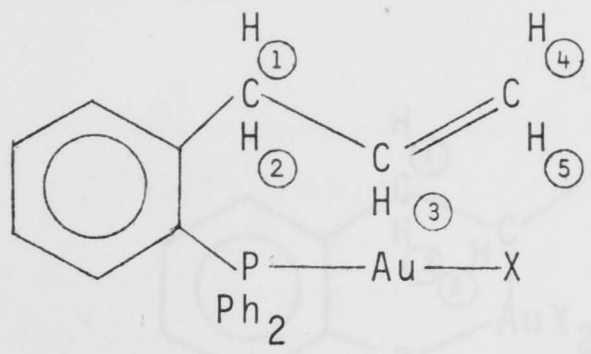
TABLE VI

Characteristic bands of the Raman spectra of the gold complexes (cm^{-1})

	$AuBr$(SP)	$AuBr_3$(SP) contains Au - CH	$AuCl$(AP)	$AuCl_3$(AP) contains Au - CH
ν(Au-Br)	215 - 225 broad m	210vs		
ν(Au-Cl)			260m-s	285m-s 310s
ν(Au-C)		565vs		570m
ν(C-Br)		685m		
ν(C-Cl)				680s
		Other bands		
	245w	245w	190m	195m
	265m	265m	225m	220m
	290m	290w		230m
		320m	330s	
		350w	395m	395vw
	415m	420w		425m
	445m	450m		455vw
	460w			485w
	495w	500m	535w	535m
	540s	540m	615m	615w
	615m	615w	645w-m	650m
	675m	670vs	685-715	
	705m	715w	broad m	
	760m	740w		860w
	785m	775w		

w = weak, s = strong, m = medium, vs = very strong, vw = very weak.

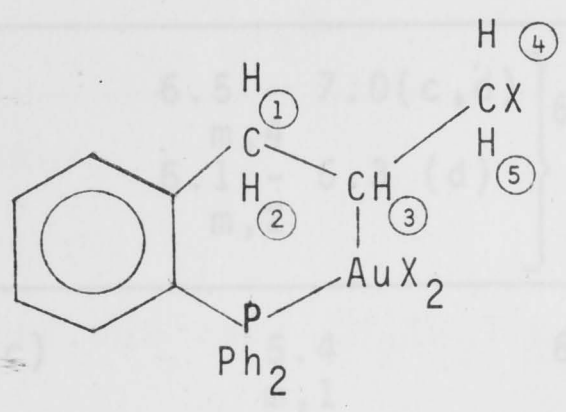
Nmr Table VII



$\tau(CDCl_3)$

	Ar	H ① H ②	H ③	H ④ H ⑤
AuBr(AP) X = Br	2.3 - 3.3 m,14	6.29 d,2	4.24 m,1 (a)	5.05 m,2 (a)
AuCl(AP) X = Cl	2.3 - 3.3 m,14	6.32 d,2	4.26 m,1 (a)	5.08 m,2 (a)

(a) Complex centre (approximate); to obtain chemical shifts requires analysis.

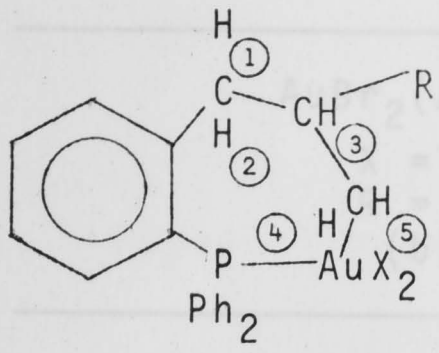


$\tau(CDCl_3)$

	Ar	H ① H ②	H ③	H ④ H ⑤
$AuBr_3$(AP) X = Br	2.0 - 3.2 m,14	6.75 m,2 (a,b)	6.38 m,1 (a)	5.26 m,2 (a)
$AuCl_3$(AP) X = Cl	2.0 - 3.2 m,14	6.86 m,2 (a,b)	6.50 m,1 (a)	5.68 m,2 (a)

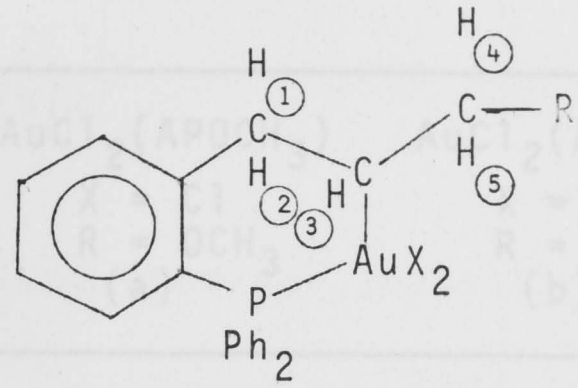
(b) The reverse assignment is possible.

Nmr Table VII



Postulated structure (e)

Less soluble isomer



Postulated structure (b)

More soluble isomer

	$AuBr_2(APOEt)$ X = Br R = OEt (a)	$AuBr_2(APOEt)$ X = Br R = OEt (b)	$AuBr_2(APOCH_3)$ X = Br R = OCH_3 (a)
Ar	2.0 - 3.2 m,14	2.0 - 3.3 m,14	2.0 - 3.3 m,14
$H_{①}$ $H_{②}$ $H_{④}$ $H_{⑤}$	6.9 - 7.4 m,4	6.5 - 7.0(c,d) m,4 6.1 - 6.3 (d) m,2	6.9 - 7.4 m,4
$H_{③}$	6.1 - 6.6(c) m,3	5.4 m,1	6.4 - 6.6(e) m,1
R	8.78 ($-CH_2CH_3$) t,3	9.02 ($-CH_2CH_3$) t,3	6.51 s,3

Nmr Table VII

	$AuBr_2(APOCH_3)$ X = Br, R = OCH_3 (b)	$AuCl_2(APOCH_3)$ X = Cl R = OCH_3 (a)	$AuCl_2(APOCH_3)$ X = Cl R = OCH_3 (b)
Ar	2.0 - 3.3 m,14	2.0 - 3.3 m,14	2.0 - 3.3 m,14
$H_{①}$ $H_{②}$	6.6 - 7.0 (d) m,2	6.7 - 7.4 m,4	6.2 - 7.3 m,4
$H_{④}$ $H_{⑤}$	6.1 - 6.3 (d) m,2		
$H_{③}$	5.35 m,1	6.4 - 6.5(e) m,1	5.5 - 5.7 m,1
R	6.86 s,3	6.52 s,3	6.87 s,3

(a) Less soluble isomer.

(b) More soluble isomer.

(c) Contains a quartet due to ($-CH_2CH_3$) of the ethoxy group.

(d) The reverse assignment for $H_{①}$ $H_{②}$ and $H_{④}$ $H_{⑤}$ is possible.

(e) The complex lies under the singlet of the methoxy protons.

CHAPTER VI

EXPERIMENTAL

A. Physical measurements and chemical analyses

B. Preparation of the platinum complexes

C. Preparation of the gold complexes

Table VIII

Table IX

Table X

EXPERIMENTAL

A. Physical measurements and chemical analyses

Infrared Spectra

Routine infrared spectra were measured on a Perkin-Elmer 457 spectrometer, solid samples as Nujol mulls and liquids as thin films unless otherwise stated.

Nuclear Magnetic Resonance Spectra

Nuclear magnetic resonance spectra were recorded at 60 and 100 MHz on JEOLCO C - 60 HL and Varian HR 100 instruments respectively. The spectra were measured using tetramethylsilane as internal standard (60 MHz) or internal lock signal (100 MHz) and were recorded in deuteriochloroform solution unless otherwise stated.

Molecular Weights and Microanalyses

Molecular weights were measured at 25°C in Analar solvents (*ca* 0.02M) using a vapour pressure osometer (Model 301 A, Mechrolab) calibrated with benzil.

Microanalyses were carried out by the John Curtin School of Medical Research (Canberra) and by the Research School of Chemistry (Canberra).

Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected.

Chemical Preparations

All solutions were evaporated to dryness or to a smaller volume under reduced pressure using a Buchi Rotavapor-R.

B. Preparation of the platinum complexes

(i) $PtBr_3$(SABr)(SA) (*3*c), (ii) $PtBr_3$(SAOEt)(SA) (*6*c), (iii) $PtBr_3$(SAOMe)(SA) (*6*c), were prepared as previously described.[4]

(iv) $PtBr_2(SA)_2$ (*2*c)

o-Styryldimethylarsine (3.29 g., 0.0158 mole) in chloroform (10 ml.) was added slowly to a stirred suspension of anhydrous platinum bromide (2.81 g., 0.0079 mole) in chloroform (40 ml.). The deep yellow solution was refluxed for twenty minutes then centrifuged to remove a black residue. On evaporation to dryness the solution gave an orange gum which solidified to a deep yellow solid on addition of benzene. This was recrystallised from benzene to give a yellow crystalline solid, probably a mixture of the *cis* and *trans* isomers, (4.8 g., 78%).

(v) $PtBr_3$(SAOH)(SA) (*19*c)

(a) by chromatography.

Unrecrystallised $PtBr_3$(SABr)(SA) (2.02 g., 0.002 mole) in benzene (50 ml.) was chromatographed on a silica gel column with benzene/acetone (ratio 3:1). A pale yellow band was eluted. This was collected and evaporated to dryness to give a yellow solid. A pale yellow crystalline solid was obtained by recrystallisation from acetone, (0.4 g., 23%).

(b) by refluxing in aqueous acetone.

Unrecrystallised $PtBr_3(SABr)(SA)$ (0.4 g., 0.00043 mole) was refluxed in acetone/water (100 ml./100 ml.) for twenty minutes. The volume of the solution was then reduced to approximately half to give a yellow solid. The yellow solid which precipitated was recrystallised from acetone, (0.1 g., 27%).

(vi) $\underline{PtBr_3(SAOH)(SA)}$ + $\underline{HBr}$.

(a) When hydrogen bromide gas was bubbled through a solution of $PtBr_3(SAOH)(SA)$ (0.2 g., 0.00023 mole) in benzene (25 ml.) for thirty minutes, a colourless oil separated which solidified overnight (*ca* 20 mg.). On evaporation to dryness this solution gave a white solid which slowly turned yellow and was shown by nmr spectra to be mainly the bromide $PtBr_3(SABr)(SA)$ (0.16 g.).

(b) Hydrobromic acid (0.18 g. of a 49% w/w solution, which is 0.00923 g. HBr, 0.0001152 mole) was added slowly to a stirred solution of $PtBr_3(SAOH)(SA)$ (0.1 g., 0.0001152 mole) in acetone (10 ml.). After stirring for 24 hours the solution was evaporated to dryness to give a yellow gum which could not be solidified.

(vii) $\underline{PtCl_2(SA)_2}$ *(23c)*.

o-Styryldimethylarsine (3.0 g., 0.0144 mole) in chloroform (10 ml.) was added slowly to a stirred suspension of platinous chloride (1.9 g., 0.0072 mole) in chloroform (20 ml.). After refluxing for thirty minutes the deep

yellow solution was centrifuged to remove a black residue, then evaporated to dryness to give a yellow gum. On addition of methanol this gum solidified and was recrystallised from methanol to give a pale yellow/green crystalline solid, (3.67 g., 75%).

(viii) $\underline{PtCl_2}(\underline{SA})_2 + \underline{Cl_2}$.

A solution of chlorine (0.31 g., 0.00433 mole) in benzene (39 g. to give an approximately 0.1 molar solution) was added slowly to a stirred solution of $PtCl_2(SA)_2$ (2.96 g., 0.00433 mole) in benzene (400 ml). After stirring for two hours and standing overnight the volume of the solution was reduced (50 ml.) and a pale green/yellow solid was filtered off, (*ca* 0.95 g.). IR and nmr spectra showed that this was the starting material.

The remainder of the solution was evaporated to dryness to give a yellow gum which recrystallised from acetone giving a pale green/yellow solid, (2.69 g.). IR and nmr spectra showed that this was mainly starting material (see Chapter III) together with a small amount of another product. Repeated recrystallisations from acetone failed to separate this product from the starting material.

C. Preparation of the gold complexes

(i) AuBr(AP) (*12*a), (ii) AuBr(SP) (*12*d),

(iii) AuCl(AP) (*13*a), (iv) AuCl(SP) (*13*d).

All were prepared following the general method for AuBr(AP)[32] except that sodium tetrachloroaurate(III) was used instead of chloroauric acid, the former giving better yields.

(v) $AuBr_3$(AP) (*15*a), (vi) $AuBr_3$(SP) (*15*d),

(vii) $AuBr_2(SPOCH_3)$ (*16*d).

All were prepared as described previously.[32]

(viii) $AuBr_2(APOCH_3)$ (*16*a).

$AuBr_3$(AP) (3.0 g., 0.004 mole) was refluxed in methanol (1500 ml.) for 1½ hours. On reduction of the volume of the solution (200 ml.) a pale green/yellow solid was obtained, (1.95 g.), which was shown by nmr spectra to contain a mixture of two isomers. Recrystallisation from benzene was carried out as described[32] to give an initial pale yellow/green precipitate (0.72 g.) (A) shown by nmr spectra to contain a mixture of the less soluble isomer and the more soluble isomer in the ratio 2:1. Evaporation of the remaining solution to dryness gave an orange solid (0.735 g.) (B) shown by nmr spectra to contain the less soluble isomer to the more soluble isomer in the ratio 1:2. Either A or B could then be further recrystallised to give pure samples of the less

soluble isomer as pale yellow/green prisms, but a pure sample of the more soluble isomer could not be obtained even by repeated recrystallisations.

(ix) $AuCl_3$(AP) (*22a*).

A saturated solution of chlorine (0.34 g., 0.0048 mole) in carbon tetrachloride (15 ml.) was added slowly to a stirred solution of AuCl(AP) (2.59 g., 0.0048 mole) in benzene (70 ml.), some yellow solid precipitating after one hour. After standing overnight the volume of the solution was reduced (40 ml.) and more yellow solid precipitated by the addition of carbon tetrachloride. This solid was recrystallised from benzene/carbon tetrachloride to give a yellow crystalline solid (1.94 g., 67%).

(x) $AuCl_3$(SP) (*22d*).

This was prepared as for $AuCl_3$(AP) using AuCl(SP) (2.5 g., 0.0048 mole) to give a pale yellow solid which was recrystallised from methanol as a colourless crystalline solid, (1.7 g., 60%).

N.B. It was found that unless dry reagents were used in this preparation, some decomposition to gold occurred during the addition of chlorine.

(xi) $AuCl_2$($APOCH_3$) (*24a*).

A white crystalline solid, consisting of the less soluble isomer only (0.66 g.), was prepared by refluxing $AuCl_3$(AP) (1.93 g., 0.00319 mole) in methanol (500 ml.) for six hours then reducing the volume of the solution

to 250 ml. Recrystallisation from methanol gave colourless plates (0.3 g.). Further reduction of the volume of the refluxed solution gave a white solid (0.4 g.) shown by nmr spectra to contain a mixture of the two isomers of (*24*a). Repeated recrystallisations of this mixture failed to give a pure sample of the more soluble isomer.

(xii) $\underline{AuCl_2(SPOCH_3)}$ *(24d)*.

A solution of $AuCl_3(SP)$ (0.3 g., 0.0005 mole) in methanol (100 ml.) was refluxed for one week. Reduction of the volume to approximately half gave white feathery crystals, (0.22 g., 80%).

(xiii) $\underline{AuCl_2(SPOCOCH_3)}$ *(25d)*.

A solution of $AuCl_3(SP)$ (0.5 g., 0.00085 mole) in glacial acetic acid (500 ml.) was refluxed for eight hours. After filtering the solution was evaporated to dryness to give a yellow solid which was recrystallised from methylene chloride/carbon tetrachloride giving a pale yellow crystalline solid, (0.314 g., 60%).

(xiv) $\underline{AuCl_3(SP)}$ + water.

A solution of $AuCl_3(SP)$ (0.22 g., 0.00037 mole) was refluxed in water/acetone (20 ml./30 ml.). After three hours a considerable amount of decomposition had occurred to give a gold deposit on the flask. The solution was therefore cooled, filtered, reduced in volume (25 ml.) and extracted with chloroform. The dried extracts were

evaporated to dryness to give a grey/white solid shown by nmr spectra to be unchanged $AuCl_3(SP)$.

(xv) $\underline{AuBr_2(SPOH)}$ *(20d)*.

$AuBr_3(SP)$ (0.3 g., 0.00041 mole) was refluxed in acetone/water (100 ml./100 ml.) for eight hours. The clear colourless solution obtained was reduced in volume (100 ml.) to give a pale yellow suspension which was extracted with chloroform. Addition of petroleum ether (40-60) to the dried extracts gave an orange solid which was recrystallised from methylene chloride/carbon tetrachloride giving a pale yellow crystalline solid, (0.12 g., 66%).

(xvi) $\underline{AuBr_2(SPOH) + HBr}$.

(a) Hydrogen bromide gas was bubbled through a solution of $AuBr_2(SPOH)$ (0.05 g., 0.000076 mole) in acetone (minimum required to dissolve the complex, *ca* 10 ml.) and carbon tetrachloride (70 ml.) for twenty minutes. After stirring for two hours a brown oil separated which slowly gave a yellow solid (one week) shown by nmr spectra to be $AuBr_3(SP)$ (0.05 g., 90%).

(b) A solution of hydrogen bromide (0.012 g., 0.00015 mole) in carbon tetrachloride (15 ml.) was added slowly to a stirred solution of $AuBr_2(SPOH)$ (0.1 g., 0.00015 mole) in carbon tetrachloride (150 ml.) After stirring for eight hours then standing overnight the solution was evaporated to dryness to give a pale yellow solid (0.1 g.) shown by nmr spectra to consist of unchanged $AuBr_2(SPOH)$ with a small amount of $AuBr_3(SP)$.

(xvii) $AuBr_2(SPOCOCH_3)$ (21d).

This was prepared as for $AuCl_2(SPOCOCH_3)$ (xiii) by refluxing $AuBr_3(SP)$ (0.2 g., 0.00026 mole) in glacial acetic acid (150 ml.) to give an orange solid. Recrystallisation from methylene chloride/carbon tetrachloride gave a pale orange crystalline solid (0.12 g., 66%).

(xviii) $AuBr_3(SP)$ + other nucleophilic reagents.

See Table IX.

None of these reactions gave products that could be positively identified.

(xix) AuBr(SP) + electrophilic reagents (other than halogens.

See Table VIII.

None of these reagents, known to be active electrophiles, appeared to react with AuBr(SP).

(xx) Attempted preparation of AuI(SP).

Sodium metabisulphite (0.71 g., 0.000375 mole) in water (2 ml.) was added slowly to an ice-cold stirred solution of sodium tetrachloroaurate(III) (3.0 g., 0.0075 mole) and lithium iodide (5.7 g., 0.037 mole) in ethanol (60 ml.). After centrifuging to remove a white precipitate the pale yellow solution was diluted to 200 ml. with ethanol then stirred at room temperature for thirty minutes to ensure that no more precipitation occurred. *o*-Styryldiphenylphosphine (2.16 g., 0.0075 mole) in ethanol (60 ml.) was added to the stirred

solution giving a white precipitate. After refluxing for one hour the solution was allowed to stand overnight. Reduction of the volume of the solution to approximately half gave a pale yellow crystalline solid, shown by analysis to be $AuI(SP)_2$ (2.18 g.).

(xxi) $\underline{AuI(SP)_2 + I_2}$.

A solution of iodine (0.2 g., 0.0008 mole) in benzene (10 ml.) was added slowly to a stirred solution of $AuI(SP)_2$ (0.72 g., 0.0008 mole) in benzene (25 ml.). The deep red solution was stirred for one hour then allowed to stand overnight. Evaporation of the solution to dryness gave a brown gum which was converted to a yellow solid by the addition of methanol. An nmr spectrum showed that this solid was probably AuI(SP).

(xxii) AuBr(SA) (12c).

A solution of sodium metabisulphite (0.48 g., 0.0025 mole) in water (2 ml.) was added slowly to a stirred ice-cold solution of sodium tetrachloroaurate(III) (2.0 g., 0.005 mole) and lithium bromide (2.17 g., 0.025 mole) in ethanol (70 ml.). After centrifuging to remove a white precipitate the solution was diluted to 150 ml. and refluxed for two hours. The pale orange solution was filtered, then a solution of *o*-styryldimethylarsine (1.04 g., 0.005 mole) in ethanol (15 ml.) added slowly to give a colourless solution.

After stirring for one hour and allowing to stand overnight, reduction of the volume of the solution to approximately half gave a white crystalline solid, (1.79 g., 56%). The compound could not be recrystallised as this caused decomposition to a grey solid.

(xxiii) AuBr(SA) + Br_2.

A solution of bromine (0.67 g., 0.0042 mole) in dry benzene (20 ml.) was added slowly to an ice-cold solution of AuBr(SA) (2.05 g., 0.0042 mole) in dry benzene (60 ml.). After stirring for one hour the solution was filtered to give a brown solid (1.78 g.) which could not be positively identified from IR or nmr spectra, (see Chapter II).

TABLE VIII

AuBr(SP) and electrophilic reagents

A	Reagent	N-bromo succinimide	N-bromo succinimide
B	Solvent	Water	Water/methanol (ratio 1:1)
C	Experimental conditions	Solution stirred at R.T. for 1 hour.	Solution stirred at R.T. for 3 hours.
D	Method of obtaining product.	Solution filtered to give ppt.	Solution evaporated to dryness.
E	Result	White solid, AuBr(SP).	Pale cream solid, AuBr(SP).

R.T. = Room temperature.

Ppt. = Precipitate.

Evap.= Evaporated.

TABLE VIII

AuBr(SP) and electrophilic reagents

A	Excess HBr gas	2,4-dinitro-phenylsulphenyl chloride	Acetyl hypobromite.[77]
B	Benzene	dichloromethane	Carbon tetrachloride.
C	Solution stirred at R.T. for 1 hour. Allowed to stand 2 days	Ice-cold solution stirred for 1 hour.	Ice-cold solution stirred for 15 mins., then at R.T. for 1 hour.
D	Solution evap. to dryness	Solution evap. to dryness to give yellow oil. This solidified on addition of benzene.	Solution filtered then solid ppt. by addition of petrol.
E	White solid, AuBr(SP)	Orange solid, (a)	Pale yellow solid, AuBr(SP).

For abbreviations and key to letters see page 164.

(a) Unknown compound which was not soluble enough in organic solvents to give reasonable nmr spectra.

TABLE IX

$AuBr_3$(SP) and nucleophilic reagents

	A	B
Nucleophilic Reagent	Dry silver acetate	Dry silver oxide
Solvent	Chloroform	Benzene
Experimental conditions	Stirred at R.T. for 1 hour.	Stirred at R.T. for 24 hours
Method of obtaining solid	Filtered to remove ppt. Soln. dried over $MgSO_4$ then evap. to dryness.	Filtered to remove ppt. Soln. evap. to dryness.
Result	Grey solid, $AuBr_3$(SP) + unknown compound.	Brown gum, thought to be oxide of SP.
Nmr parameters of product.	Resonances due to $AuBr_3$(SP) + m, 6.0τ, s, 7.88τ, s, 8.72τ.	m, 2.2τ - 3.1τ(Ar,15) dd, 4.34τ, 4.52τ, 4.82τ, 4.92τ. (?, 2)

R.T. = Room temperature.

Evap. = Evaporated.

Soln. = Solution.

Ppt. = Precipitate.

TABLE IX

$AuBr_3$(SP) and nucleophilic reagents

A	Excess phenol	Silver tosylate (undried)	Silver tosylate (dried)
B	Acetone	Acetone	Acetone
C	Refluxed for 3 hours	Stirred at R.T. for 1 hour	Stirred at R.T. for 1 hour
D	Soln. evap. to oil. Washed with alkali. Extracted with $CHCl_3$. Dried over $MgSO_4$. Evap. to dryness.	Filtered to remove ppt. Evap. to dryness to give yellow oil. Dissolved in $CHCl_3$. Solid ppt. by addition of petrol.	Filtered to remove ppt. Evap. to dryness to give yellow gum. Dissolved in $CHCl_3$. Solid ppt. by addition of CCl_4.
E	Black gum which was discarded	Pale grey/green solid. $AuBr_2$(SPOH) + unknown compound	White solid Trace of $AuBr_2$(SPOH) + unknown compound.
F	No nmr spectrum obtained	Resonances due to $AuBr_2$(SPOH) + m, 4.6τ-6.5τ, s, 7.62τ.	Resonances due to $AuBr_2$(SPOH) + m, 4.6τ-6.5τ, s, 7.37τ, s, 7.62τ.

For abbreviations and key to letters , see page 166.

TABLE X

Molecular Weights and Analyses

	(*21*d)	$AuI(SP)_2$	(*23*c)	(*19*c) (a)	(*19*c) (b)	(*3*c)
C Found	37.5	52.5	35.2	29.4	28.5	25.7
C Calc.	37.5	53.4	35.0	27.7	27.7	25.8
H Found	3.1	3.8	3.8	3.3	3.5	2.8
H Calc.	2.9	3.8	3.9	3.1	3.1	2.8
Halogen Found	22.2	14.9	9.9	29.4	20.5	34.4
Halogen Calc.	22.7	14.1	10.4	27.6	27.6	34.3
Melting Point ^{o}C	184	168	180	166	167	138
Molecular Weight Found	676	539	667	777		850
Molecular Weight Calc.	704	900	682	868		931

(a) Prepared by chromatography and probably contains benzene of crystallisation.
i.e. $PtBr_3(SAOH)(SA).\ ½C_6H_6$ requires C = 30.5; H = 3.3, Br = 26.6.

(b) Prepared by refluxing the bromide in aqueous acetone. Cannot be recrystallised without decomposition occurring.

See pages 41, 85 and 104
for numbering system of compounds.

TABLE X

Molecular Weights and Analyses

	(22d)	(24d)	(22a) (c)	(24a)	(25d)	(20d)
C Found	41.4	43.0	41.6	44.1	41.8	36.2
C Calc.	40.6	42.9	37.8	43.9	42.9	36.2
H Found	2.8	4.46	2.9	4.1	3.3	2.9
H Calc.	2.9	3.4	3.1	3.7	3.4	2.7
Halogen Found	17.5	12.1	15.9	10.7	12.5	25.4
Halogen Calc.	18.0	12.1	17.6	11.8	12.1	24.1
Melting Point ^{o}C	213	223	180	180	223	153
Molecular Weight Found	658	607	569	583	573	669
Molecular Weight Calc.	590	587	605.5	601	615	662

(c) Probably contains benzene of crystallisation,

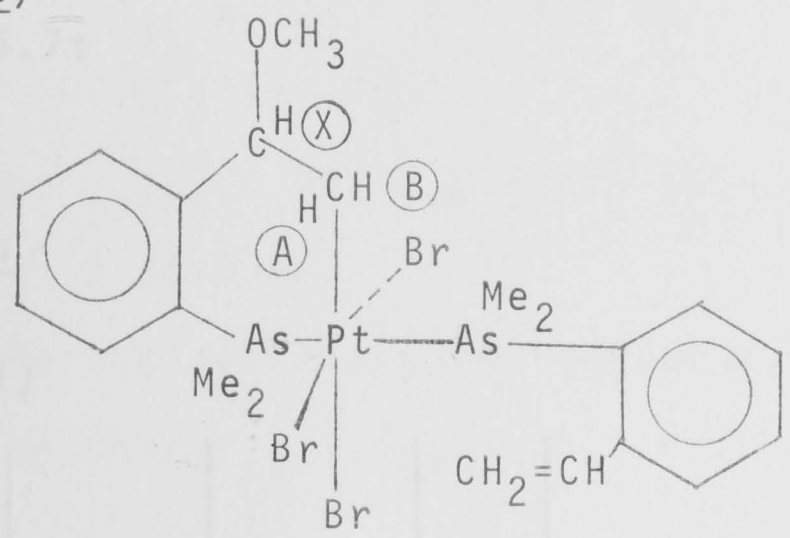
i.e. $AuCl_3(AP)$. C_6H_6 requires C = 47.4, H = 3.6.

See pages 85 and 104 for numbering system of compounds.

APPENDIX

As explained in Chapter II the nmr spectra of the chelate ring protons in some of the six membered chelate ring complexes show patterns characteristic of an ABX system. To find the chemical shifts and coupling constants of the protons in these chelate rings the second order patterns were analysed by a graphical method.[84] A typical example will now be worked through to show how this method is applied.

Analysis of the pattern due to the chelate ring protons in $PtBr_3$(SA)(SAOMe)



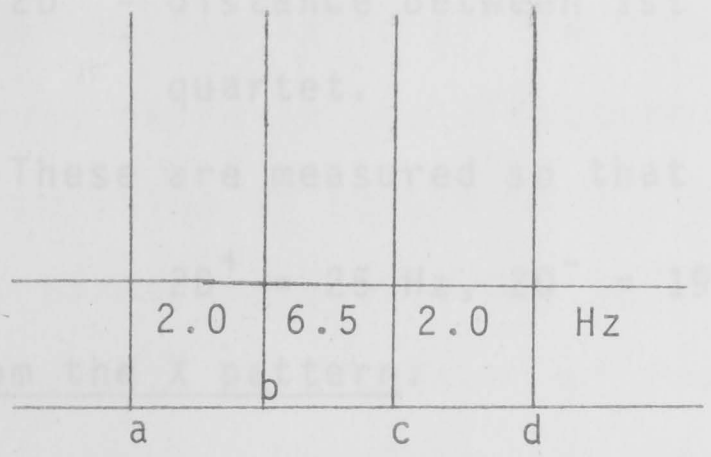
The ^{195}Pt decoupled 100 MHz nmr spectrum of the chelate ring protons shows a complex resonance at *ca* 5.7τ consisting of four peaks due to H_X and another complex resonance at *ca* 7.0τ. The latter shows eight peaks due to H_A and H_B, two of the peaks overlapping the singlet of the methoxy protons. This ABX pattern is shown on page 171, the distance between each peak being given in Hertz. The eight peaks due to H_A and H_B are supposed to consist of two overlapping quartets due to H_A and H_B respectively.

i.e. either (1) H_A - f,h,j,l. H_B - e,g,i,k.

or (2) H_A - e,f,j,l. H_B - g,h,i,k.

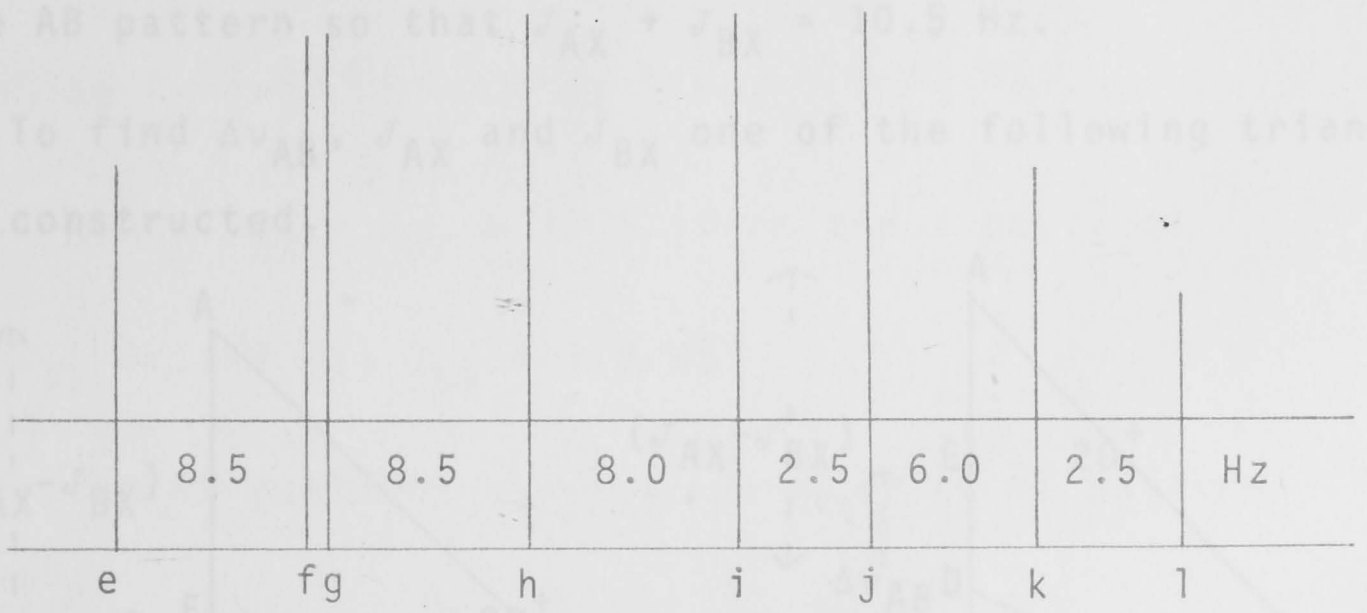
Nmr pattern due to the chelate ring protons in $PtBr_3(SAOMe)(SA)$.

(1) X Pattern



ca 5.7τ

(2) AB Pattern



ca 7.0τ

(i) Lie under singlet due to methoxy proton therefore position only approximate.

Alternative (1) will now be considered:-

From the AB pattern.

J_{AB} = eg = fh = ik = jl = 8.5 Hz

$2D^+$ = distance between 1st and 3rd peaks of one quartet.

$2D^-$ = distance between 1st and 3rd peaks of the other quartet.

These are measured so that $2D^+ > 2D^-$.

$2D^+$ = 25 Hz, $2D^-$ = 19 Hz.

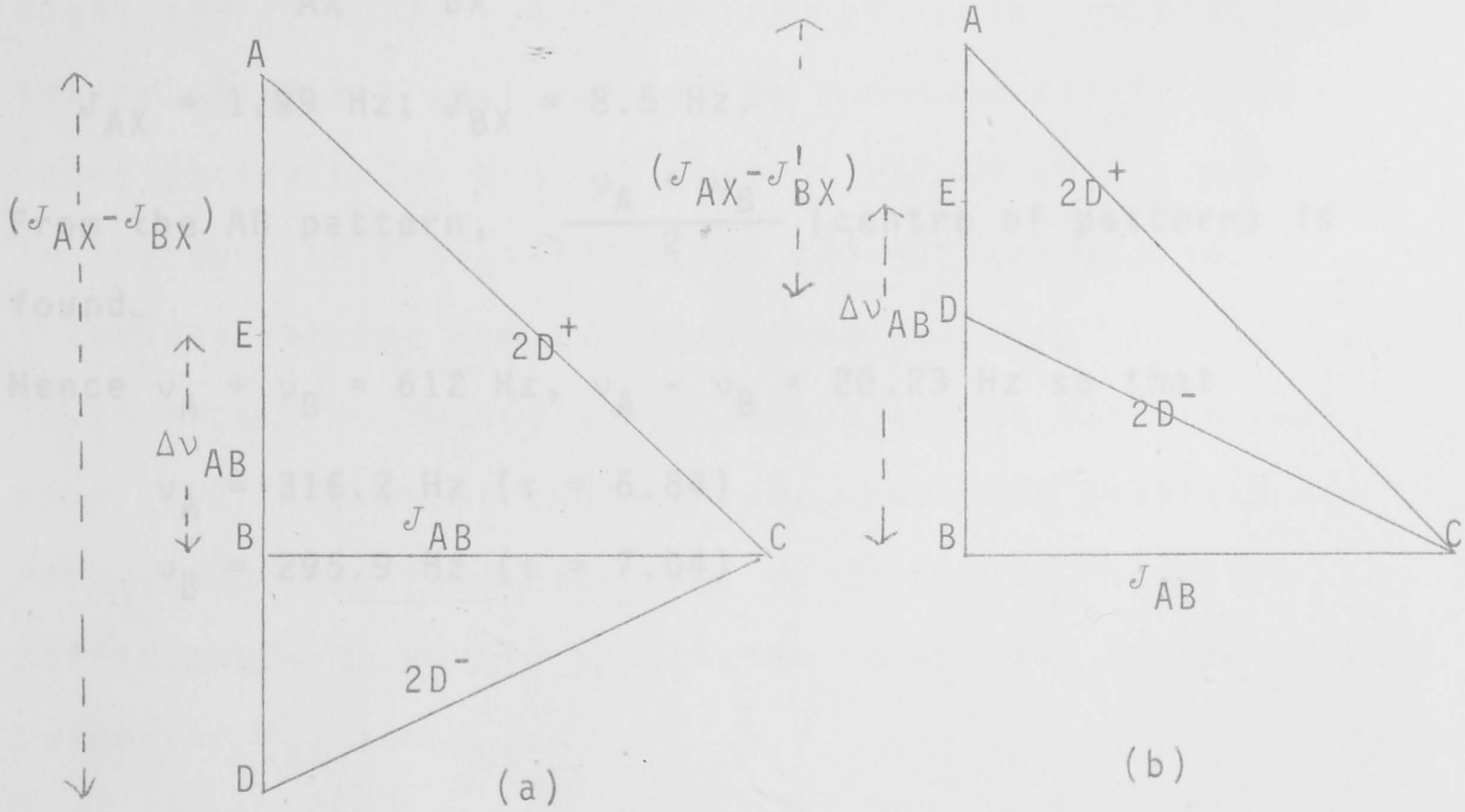
From the X pattern.

either (i) bc = $J_{AX} + J_{BX}$ = 6.5 Hz, ad = $2D^+ - 2D^-$
= 10.5 Hz

or (ii) bc = $2D^+ - 2D^-$ = 6.5 Hz, ad = $J_{AX} + J_{BX}$
= 10.5 Hz.

In this case alternative (ii) gives better agreement with the AB pattern so that $J_{AX} + J_{BX}$ = 10.5 Hz.

To find $\Delta\nu_{AB}$, J_{AX} and J_{BX} one of the following triangles is constructed.



The correct triangle is chosen by considering the X pattern and the angle ACD in (a) and (b). The X pattern can vary from six peaks consisting of two strong peaks, two medium peaks and two weak peaks to four peaks of almost equal intensity. In the triangles (a) and (b) $(\cos < ACD)^2$ is equal to the ratio of the intensities of the medium to the strong peaks in the X pattern. Therefore (a), having a large value of $(\cos < ACD)^2$, represents an X pattern of six peaks while (b), having a small value of $(\cos < ACD)^2$, represents an X pattern of four peaks of almost equal intensity. The latter is true for $PtBr_3(SAOMe)(SA)$ and if (b) is constructed it is found that;

$$(\cos < ACD)^2 = 0.996 = \frac{\text{intensity of medium peaks}}{\text{intensity of strong peaks}}$$

From triangle (b) the following are found:-

$\Delta\nu_{AB} = 20.23$ Hz $\qquad J_{AX} - J_{BX} = 6.51$ Hz

Also since $J_{AX} + J_{BX} = 10.5$ (from the X pattern)

$J_{AX} = 1.99$ Hz; $J_{BX} = 8.5$ Hz.

From the AB pattern, $\frac{\nu_A + \nu_B}{2}$ (centre of pattern) is found.

Hence $\nu_A + \nu_B = 612$ Hz, $\nu_A - \nu_B = 20.23$ Hz so that

$\nu_A = 316.2$ Hz ($\tau = 6.84$)

$\nu_B = 295.9$ Hz ($\tau = 7.04$)

If the alternative allocation (2) is followed, the following results are obtained:- J_{AB} = 8.5 Hz, J_{AX} = 9.25 Hz, J_{BX} = -2.75 Hz, ν_A = 316 Hz, ν_B = 296 Hz. Since the most probable allocation cannot be decided from the observed spectrum both sets of results must be considered. It has been shown however that vicinal proton-proton coupling constants are usually positive.[85] Two methods can be used to find the most probable sets of results:-

(1) The calculated values obtained for the chemical shifts and coupling constants can be confirmed by using a computor to simulate the Lorentzian envelope of the AB and X parts of the ABX pattern. In the present work the program was run on an 8K PDP8/I computor connected to a Hewlett Packard 4200A graphic plotter. For the same compound each alternative set of results gives patterns that differ only in the intensity of the peaks (see pages 178 to 183). A comparison of these patterns with the original nmr spectrum of the compound can in some cases decide which are the correct values of J_{AX} and J_{BX}. In the case of $PtBr_3$(SAOMe)(SA) the differences in intensity between the two simulated patterns are not large enough to decide which assignment is correct (see page 179). However the simulated patterns obtained for $PtBr_3$(SAOH)(SA) (see page 178) do differ in intensity sufficiently to enable a decision to be made on the correct values of J_{AX} and J_{BX}.

(2) If the complex is soluble enough, spin tickling techniques can be carried out on a concentrated solution of the sample to determine the sign of the coupling constant. This technique could be used on all complexes except $PtBr_3(SAOH)(SA)$, which was not soluble enough, and it was found that both J_{AX} and J_{BX} are positive. All results, together with the alternative values calculated for J_{AX} and J_{BX}, are given in Table XI.

TABLE XI

ABX analysis of the chelate ring protons

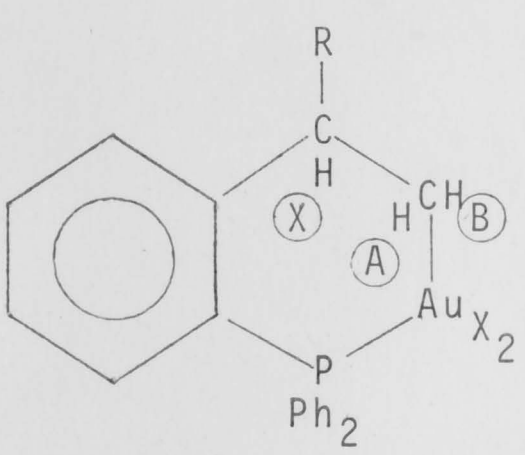
	^{J}AB Hz	^{J}BX Hz	^{J}AX Hz	ν_B τ	ν_A τ	^{J}BX Hz	^{J}AX Hz
1.	10.0	5.4	1.6	6.65	6.76	6.3	-3.3
2.	8.5	8.5	2.0	6.84	7.04	9.3	-2.8
3.	8.3	9.8	1.7	6.86	7.15	10.1	-2.6
4.	12.3	4.6	2.7	5.17	5.43	5.2	-3.4
5.	12.5	4.3	3.2	5.59	6.07	4.6	-3.1
6.	11.8	5.3	2.5	5.50	5.97	5.4	-2.6

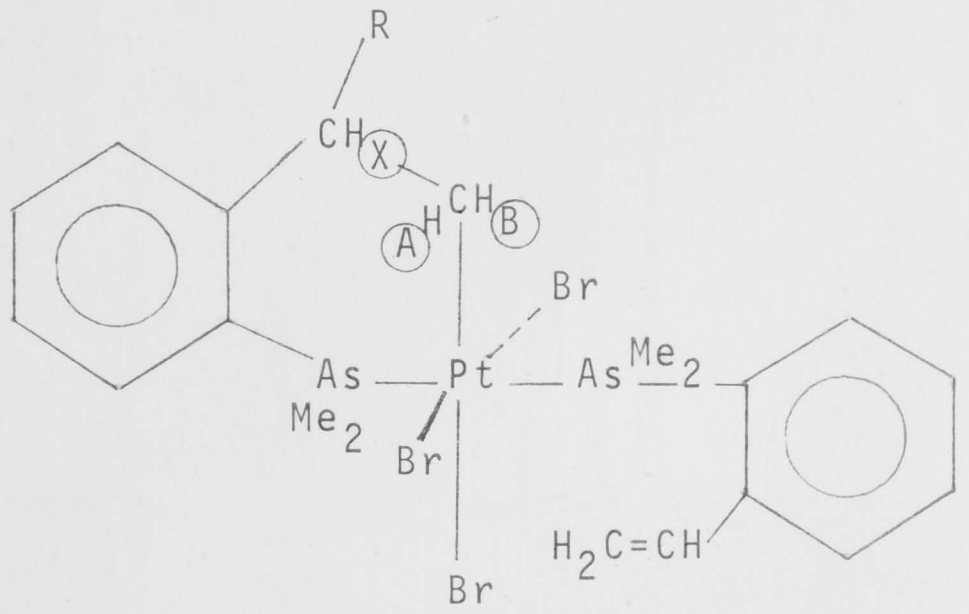
Key to compounds. 1. $PtBr_3(SAOH)(SA)$, R = OH.

2. $PtBr_3(SAOMe)(SA)$, R = OMe. 3. $PtBr_3(SAOEt)(SA)$, R = OEt.

4. $AuBr_2(SPOCOCH_3)$, X = Br, R = $OCOCH_3$.

5. $AuBr_2(SPOH)$, X = Br, R = OH. 6. $AuCl_3(SP)$, X = Cl, R = Cl.





Key to diagrams on pages 178 to 183

1. The 100 MHz proton nmr spectrum of the compound. The spectra of the gold complexes are ^{31}P decoupled and those of the platinum complexes are ^{195}Pt decoupled.

   N.B. In the nmr spectrum of $PtBr_3(SAOMe)(SA)$ (page 179) the singlet due to the methoxy protons obscures part of the AB pattern.

2. Computed spectrum assuming both J_{AX} and J_{BX} are positive.

3. Computed spectrum assuming J_{AX} is negative.

$PtBr_3(SAOH)(SA)$

X pattern

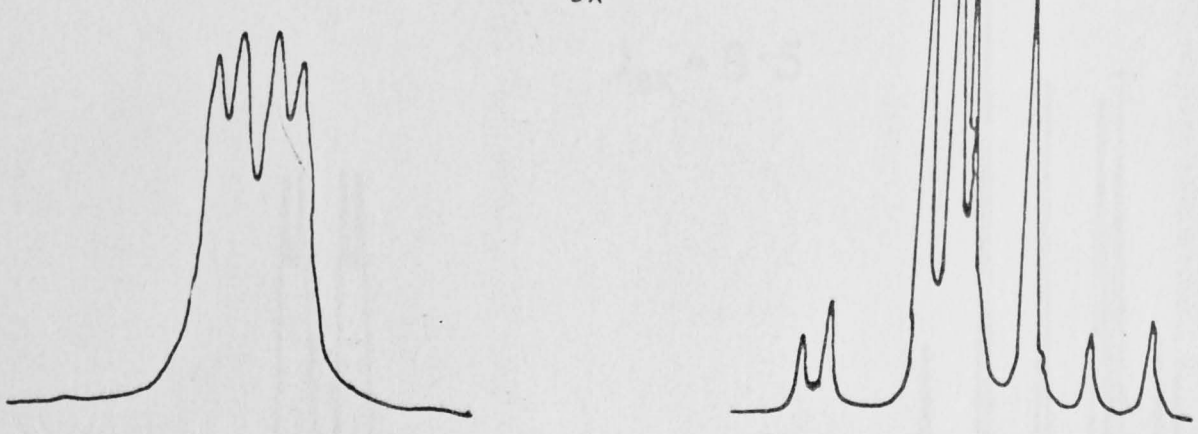
AB pattern

1.

$J_{AX} = 1{\cdot}6$

$J_{BX} = 5{\cdot}4$

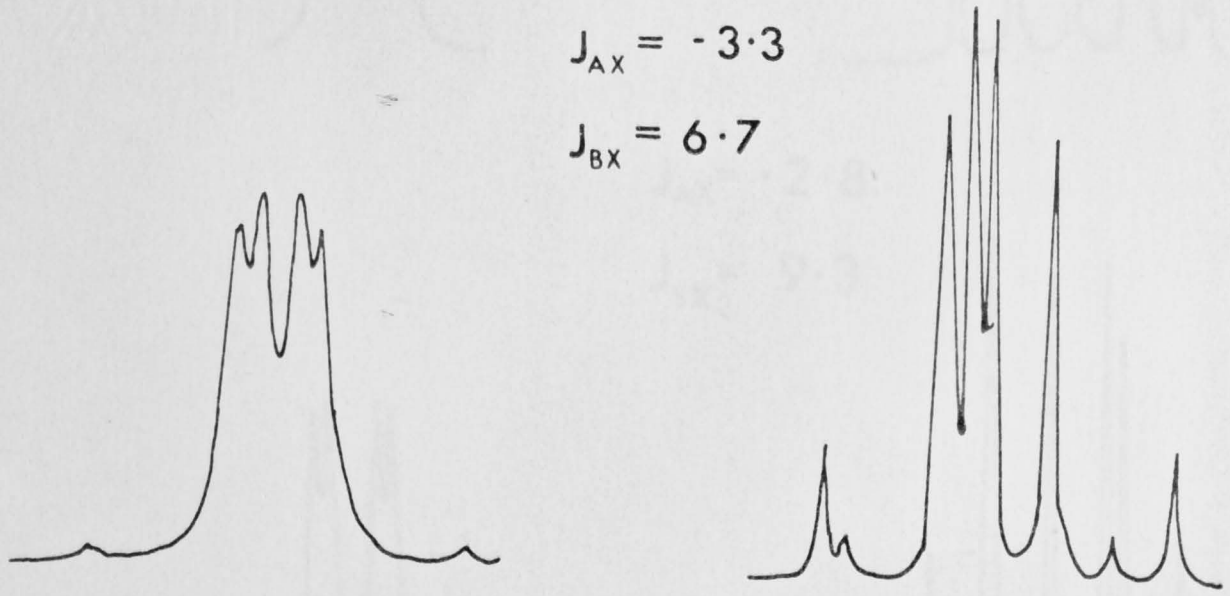
2.



$J_{AX} = -3{\cdot}3$

$J_{BX} = 6{\cdot}7$

3.

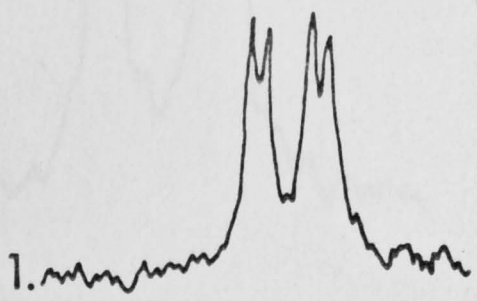


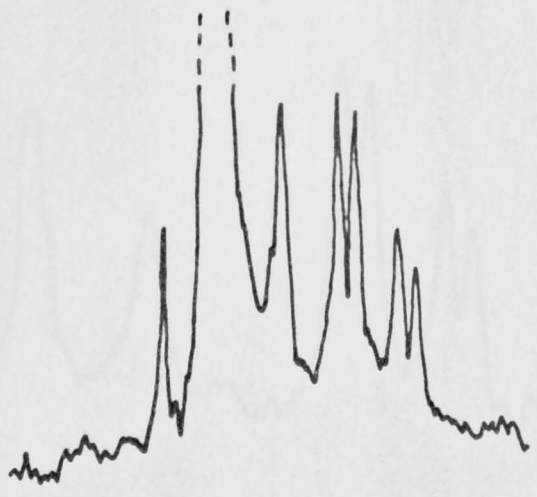
$PtBr_3(SAOMe)(SA)$

X pattern

AB pattern

1.

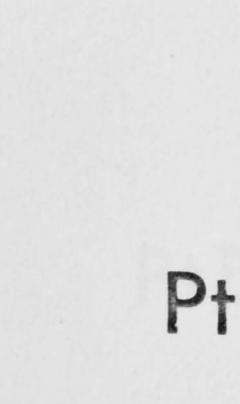




$J_{AX} = 2 \cdot 0$

$J_{BX} = 8 \cdot 5$

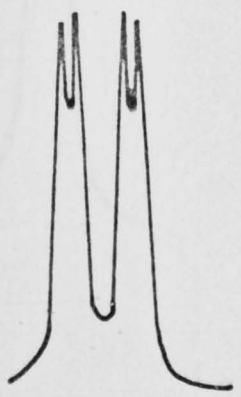
2.

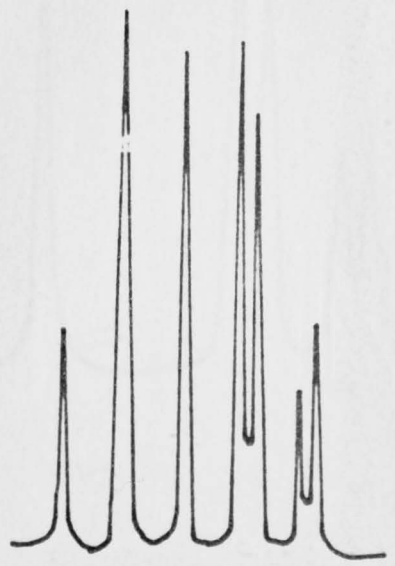


$J_{AX} = -2 \cdot 8$

$J_{BX} = 9 \cdot 3$

3.



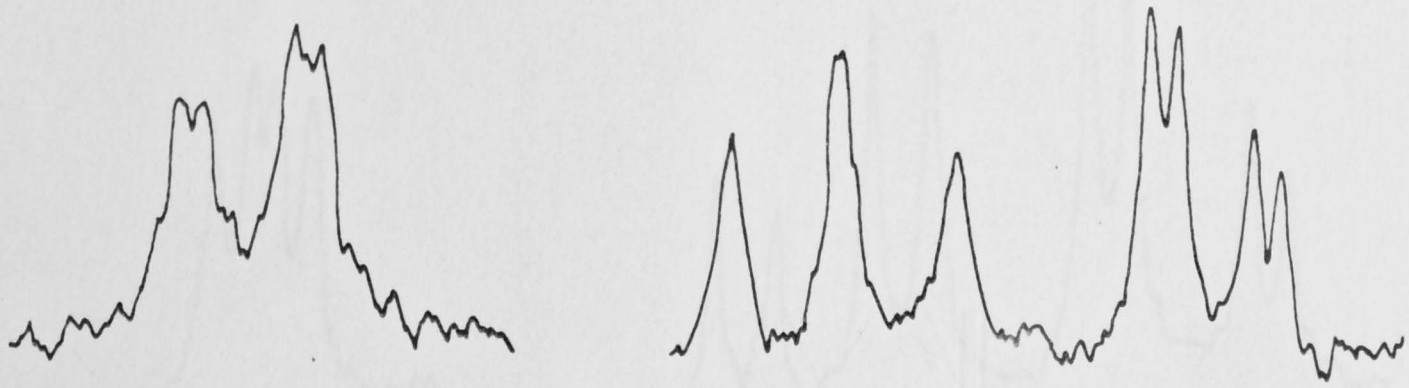


$PtBr_3(SAOEt)(SA)$

X pattern

AB pattern

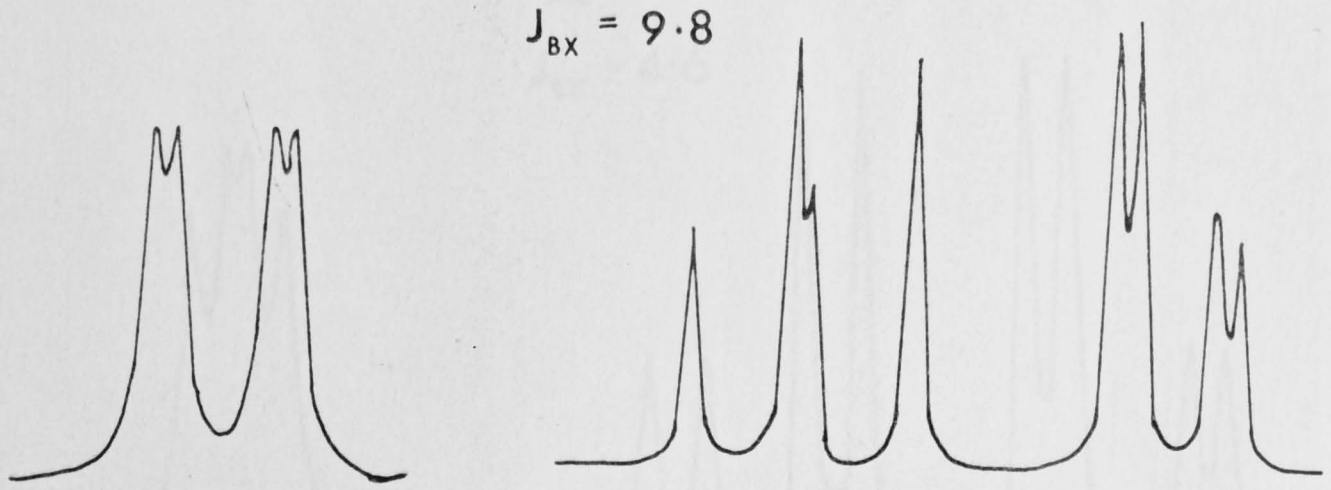
1.



$J_{AX} = 1{\cdot}7$

$J_{BX} = 9{\cdot}8$

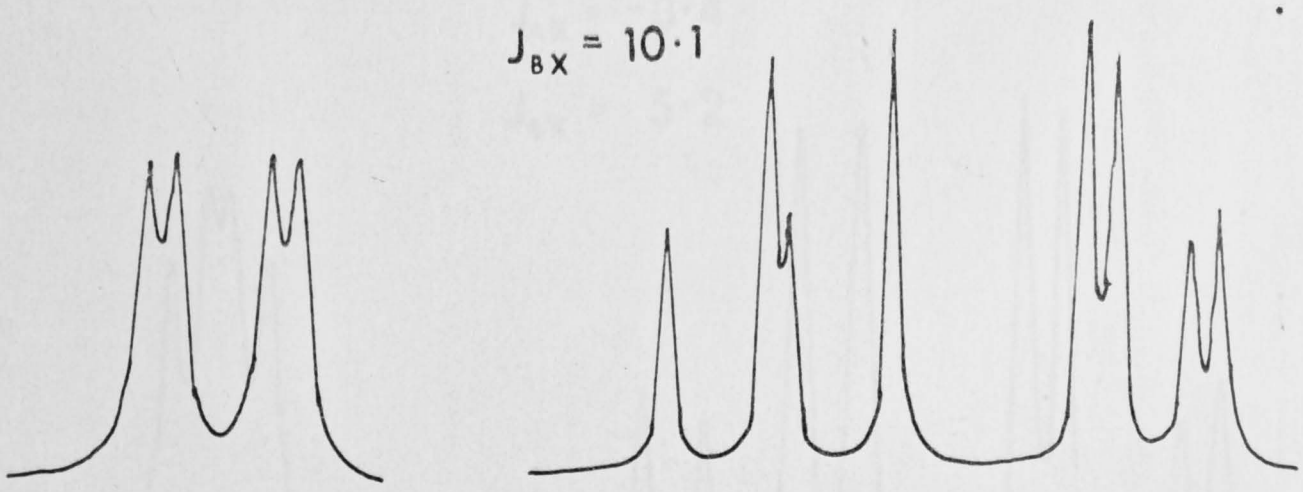
2.



$J_{AX} = -2{\cdot}6$

$J_{BX} = 10{\cdot}1$

3.

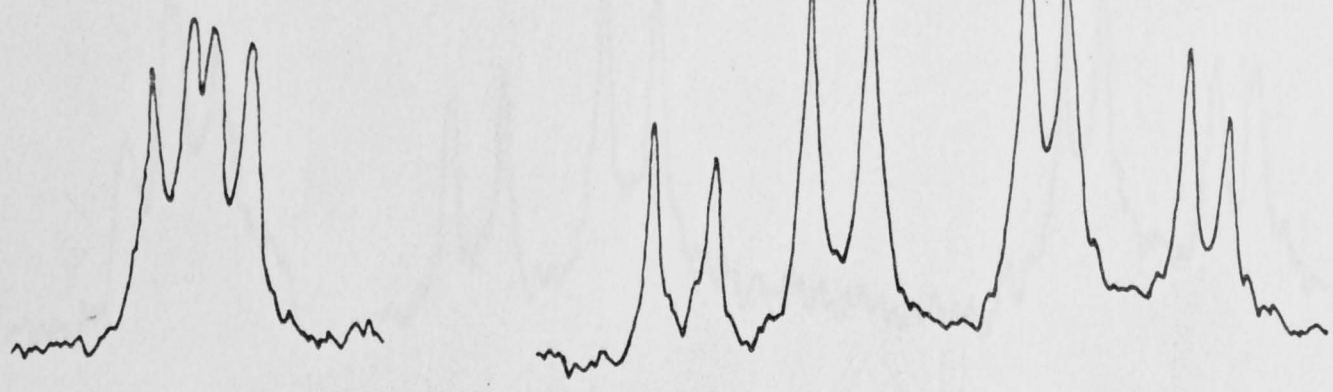


$AuBr_2(SPOCOCH_3)$

X pattern

AB pattern

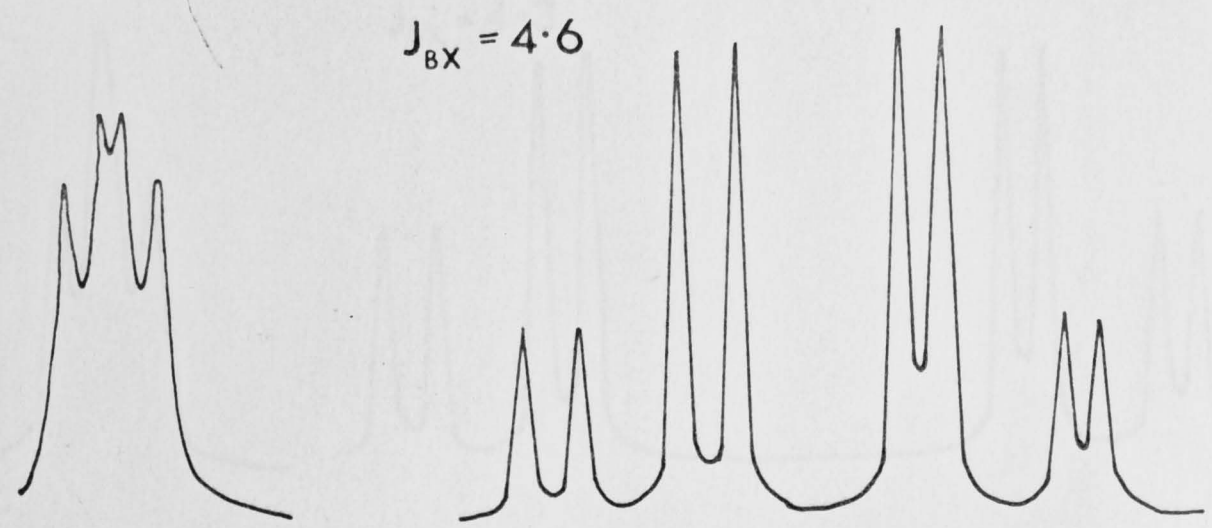
1.



$J_{AX} = 2{\cdot}7$

$J_{BX} = 4{\cdot}6$

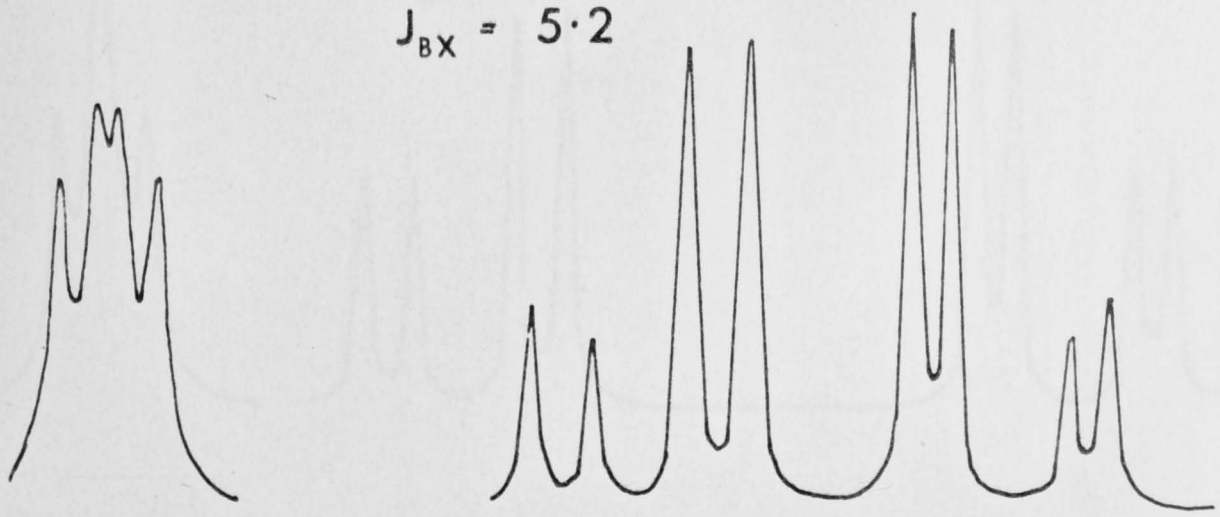
2.



$J_{AX} = -3{\cdot}4$

$J_{BX} = 5{\cdot}2$

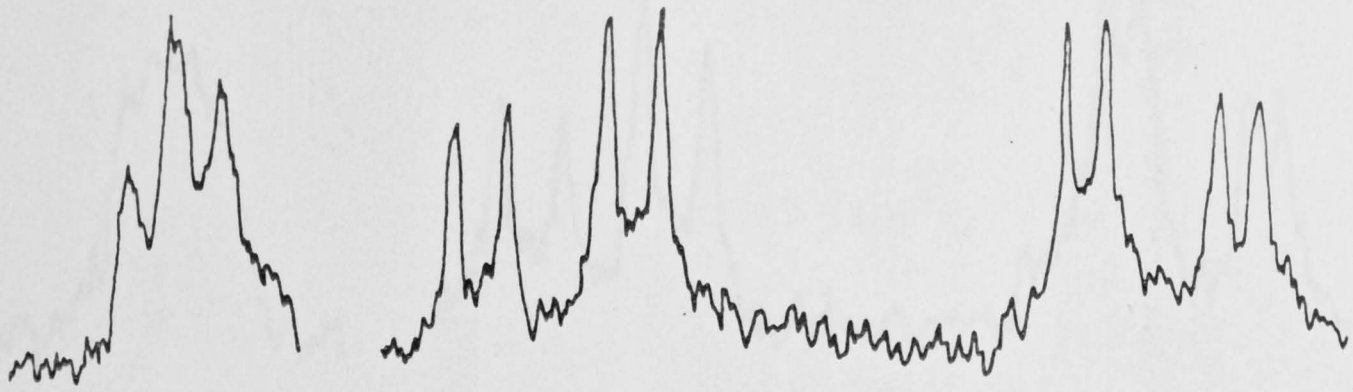
3.



$AuBr_2(SPOH)$

X pattern AB pattern

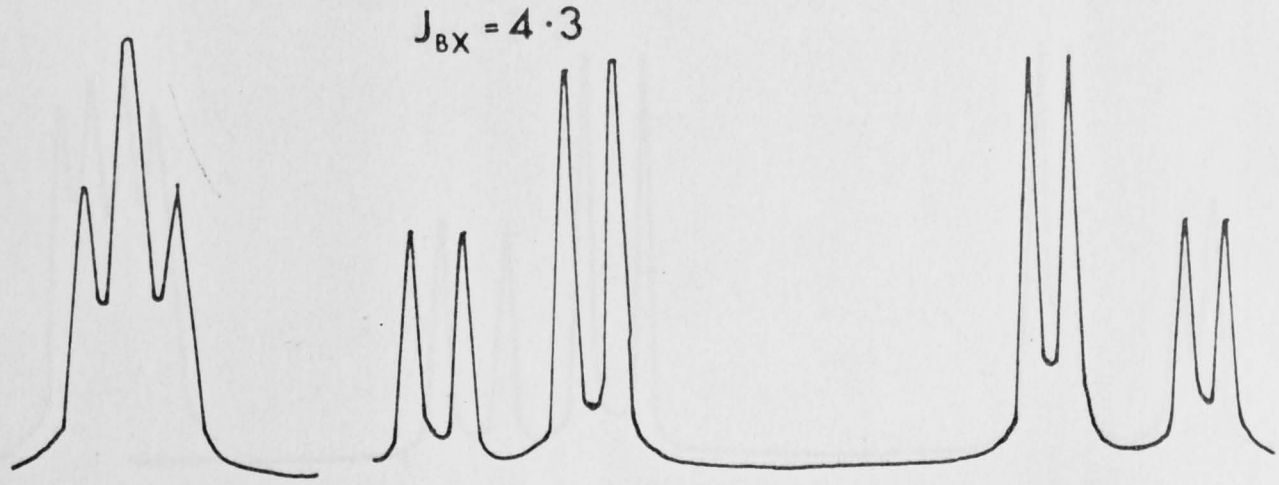
1.



$J_{AX} = 3 \cdot 2$

$J_{BX} = 4 \cdot 3$

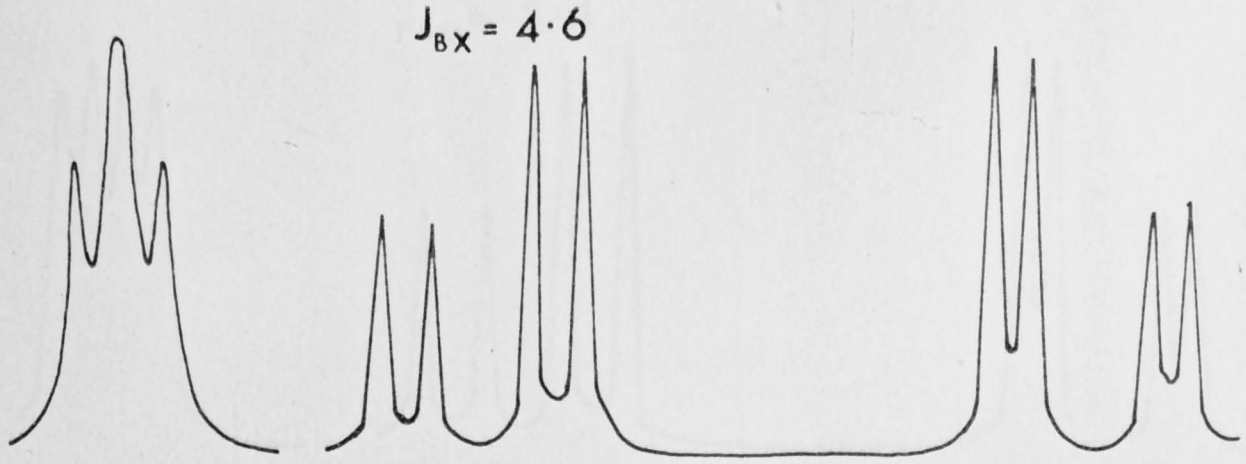
2.



$J_{AX} = -3 \cdot 1$

$J_{BX} = 4 \cdot 6$

3.

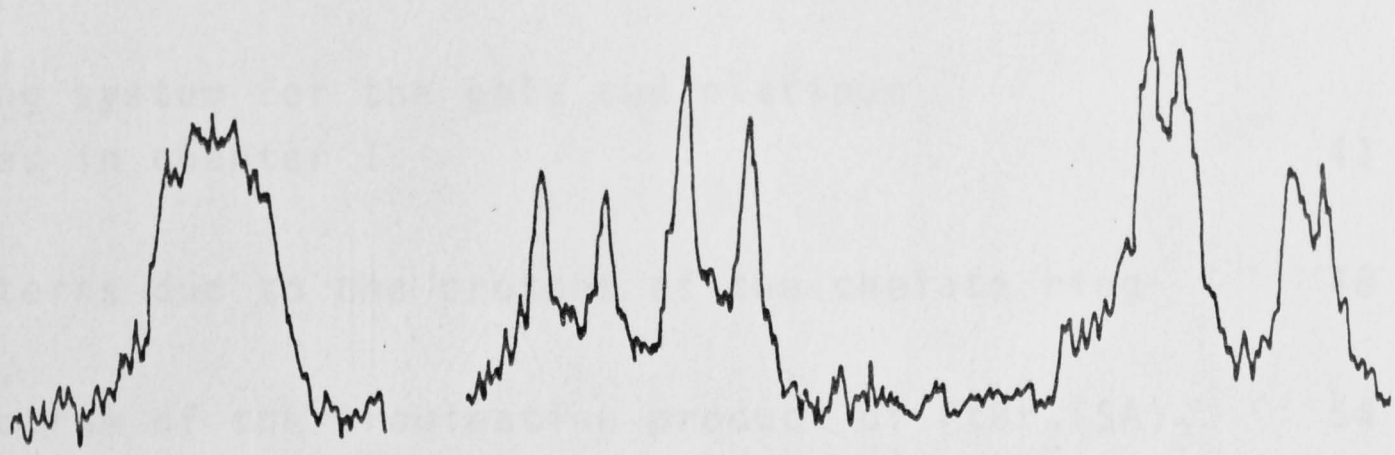


$AuCl_3(SP)$

X pattern

AB pattern

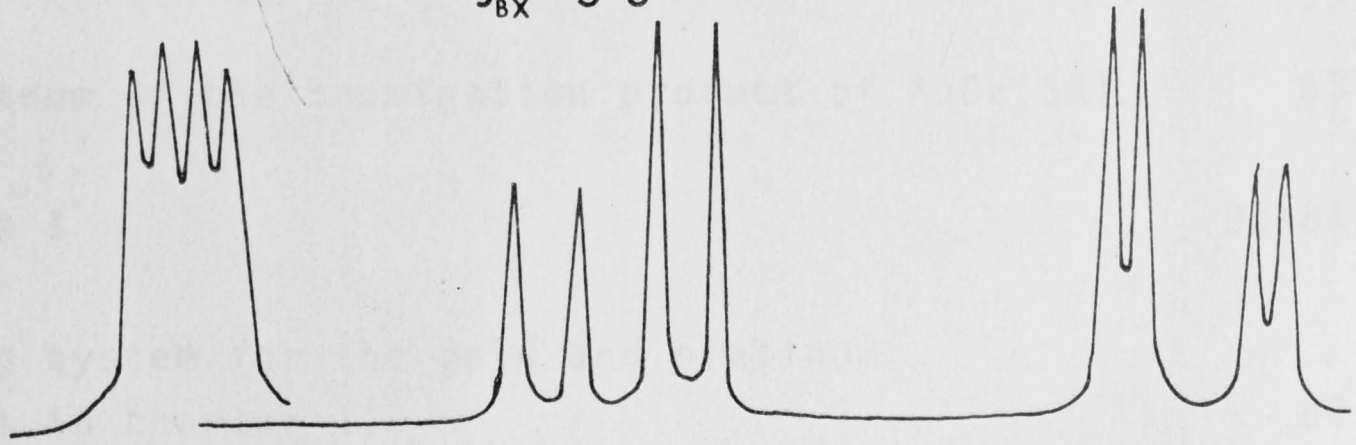
1.



$J_{AX} = 2 \cdot 5$

$J_{BX} = 5 \cdot 3$

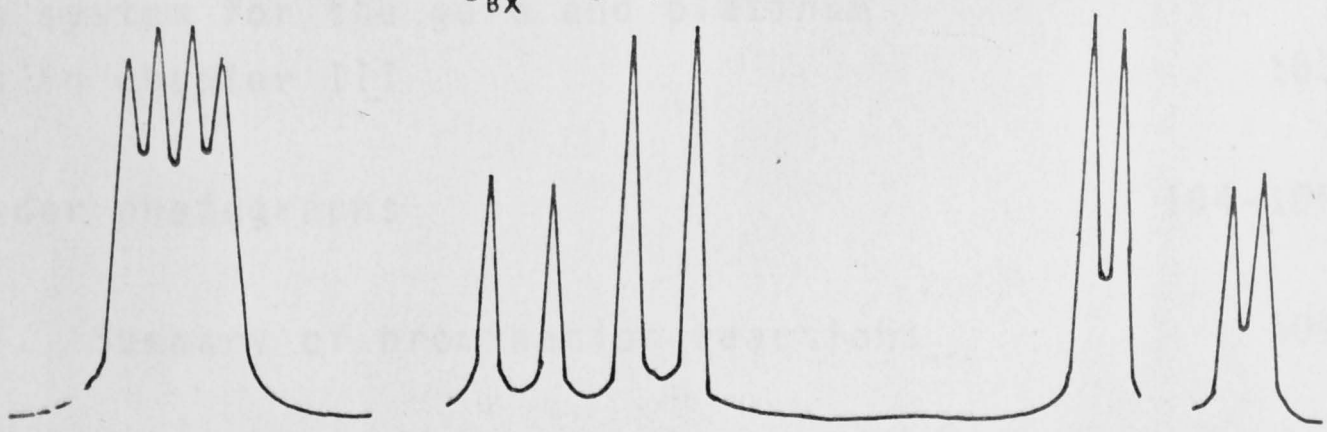
2.



$J_{AX} = -2 \cdot 6$

$J_{BX} = 5 \cdot 4$

3.



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